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THE UNIVERSITY OF ALBERTA

SYNTHESIS AND REACTIVITY OF CYCLOHEPTATRIENYL-
BRIDGED HETEROBIMETALLIC COMPLEXES.

by

STEPHEN THOMAS ASTLEY



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND
RESEARCH IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING, 1990



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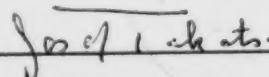
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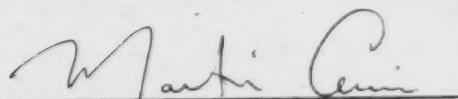
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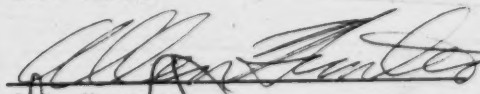
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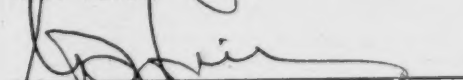


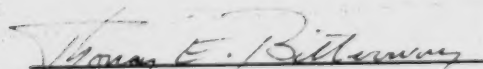
Supervisor, J. Takats


M. Cowie


S.W. Wanke


A.D. Hunter


H.J. Liu


T. Bitterwolf
External Examiner

Date November 20, 1989

Abstract.

The utility of the anionic complexes, $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Ru}, \text{Os}$) for the preparation of cycloheptatrienyl bridged heterobimetallic compounds has been investigated.

Thus, $(\eta^3\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3^-$ reacts with $[\text{Ir}(\text{COD})\text{Cl}]_2$ ($\text{COD} = 1,5$ cyclooctadiene) to give *cis*- $(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{COD})$, which contains a Ru-Ir bond with both Ru and Ir bonded to the same face of the seven-membered ring. Displacement of the COD ligand from Ir by CO yielded *cis*- $(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$. The latter compound reacts with dpmm to give *cis*- $(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)(\mu\text{-dpmm})\text{Ru}(\text{CO})_2\text{Ir}(\text{CO})$, and with PPh_3 via substitution of CO at Ir. This completed a series of complexes, *cis*- $(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{CO})\text{PPh}_3$ ($\text{M} = \text{Fe}, \text{Ru}$; $\text{M}' = \text{Rh}, \text{Ir}$) in which the rate of intermetallic carbonyl exchange increases upon descending a triad for M and M'.

In contrast to the reactivity of the anionic Ru complex, $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ reacts with the transition metal electrophiles $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) to give initially, the unsaturated trans cycloheptatrienyl bridged heterobimetallic complexes *trans*- $(\mu\text{-}\eta^4, \eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{M}(\text{COD})$ in which the two metals are on opposite faces of the C_7H_7 ligand. The trans OsRh complex was isolated and fully characterized. Interestingly it undergoes isomerization to give its coordinatively saturated *cis* isomer, which contains a metal-metal bond. In addition, the trans OsRh complex reacts rapidly with

dppm to give the *cis* dppm bridged complex $(\mu\text{-}\eta^3,\eta^4\text{-C}_7\text{H}_7)(\mu\text{-dppm})\text{Os}(\text{CO})_2\text{Rh}(\text{CO})$.

In order to probe the reasons for the different reactivity of the anionic Ru and Os complexes, $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$, the solid-state and solution structure (of the AsPh_4^+ salt) of the two complexes were investigated. It was found that the ground state structure of both complexes contains an η^3 -bonded C_7H_7 ring. This was taken to imply that subtle differences in the metal to $(\eta^3\text{-C}_7\text{H}_7)$ ligand bonding may account for the observed differences in reactivity.

The reactivity of *cis*- $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ and *cis*- $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ toward alkynes [hexafluoro-2-butyne (HFB), acetylene] was also investigated and proved to be both metal and alkyne dependent. The RuRh complex reacts at room temperature with HFB by addition of one alkyne unit. In contrast, the reaction of the RuIr complex with HFB requires thermal activation and results in CO substitution via the uptake of two HFB molecules. A similar reaction occurs between the RuRh complex and C_2H_2 at room temperature. In all three cases, alkyne insertion between Ru and the C_7H_7 ring occurred.

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List of Abbreviations

AGDP	anisotropic Gaussian displacement parameter
br	broad
Bu	butyl (C_4H_9)
^t Bu	tert-butyl [$C(CH_3)_3$]
C.I.	chemical ionization
CHT	cycloheptatriene (C_7H_8)
COD	1,5-cyclooctadiene
COT	cyclooctatetraene (C_8H_8)
Cp	cyclopentadienyl (C_5H_5)
Cp*	pentamethylcyclopentadienyl (C_5Me_5)
Cp'	methylcyclopentadienyl (C_5H_4Me)
d	doublet
dippe	1,2-bis(diisopropylphosphino)ethane
dmad	dimethyl acetylenedicarboxylate [$C_2(CO_2CH_3)_2$]
dppm	bis(diphenylphosphino)methane [$(Ph_2P)_2CH_2$]
E.I.	electron impact
Et	ethyl
FAB	fast atom bombardment
Fv	fulvalene
HFB	hexafluoro-2-butyne
IR	infrared
m	medium (with reference to IR spectra)
m	multiplet (with reference to NMR spectra)
m.p.	melting point

MS	mass spectrometry
Me	methyl
NBD	norbornadiene (C_7H_8)
NMR	nuclear magnetic resonance
Ph	phenyl
PPM	parts per million
PPN	bis(triphenylphosphoranylidene)ammonium $[(Ph_3P)_2N]^+$
iPr	iso-propyl $[CH(CH_3)_2]$
q	quartet
s	strong (with reference to IR spectra)
s	singlet (with reference to NMR spectra)
sp	septet
t	triplet
THF	tetrahydrofuran
TMS	tetramethylsilane $[Si(CH_3)_4]$
w	weak
v	very

Chapter 1

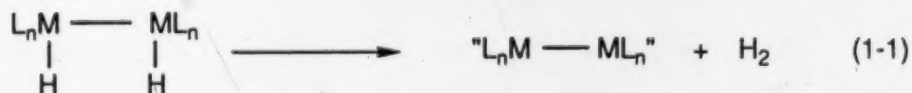
Introduction.

1.1. Background to Dinuclear Transition metal Chemistry.

In the framework of organotransition metal chemistry, bimetallic compounds occupy a central position bridging the chemical properties of mononuclear transition metal compounds and transition metal clusters (and metal surfaces). For this reason, fundamental studies on bimetallic complexes are essential to obtain a global understanding of the bonding, reactivity and applications offered by transition metal organometallic compounds.

Probably the most important industrial application of transition metal compounds today is in catalysis¹. In this regard, it is hoped that the chemistry of dinuclear complexes may combine the properties of metal-surfaces (used in heterogeneous catalysis) and soluble mononuclear transition metal complexes (widely used as homogeneous catalysts). Hence, the presence of adjacent metal sites coupled with the ability to dissolve in organic solvents may provide special reactivity which is not seen in mononuclear complexes. The ultimate goal of such studies is to provide a smooth and logical progression from the chemistry of mononuclear compounds through bimetallic compounds to metal clusters and ultimately to metal surfaces².

Two of the many useful chemical transformations currently known to occur through bimetallic compounds are C-C coupling, and dinuclear reductive elimination of H_2 (equation 1-1)³. Additionally, there are

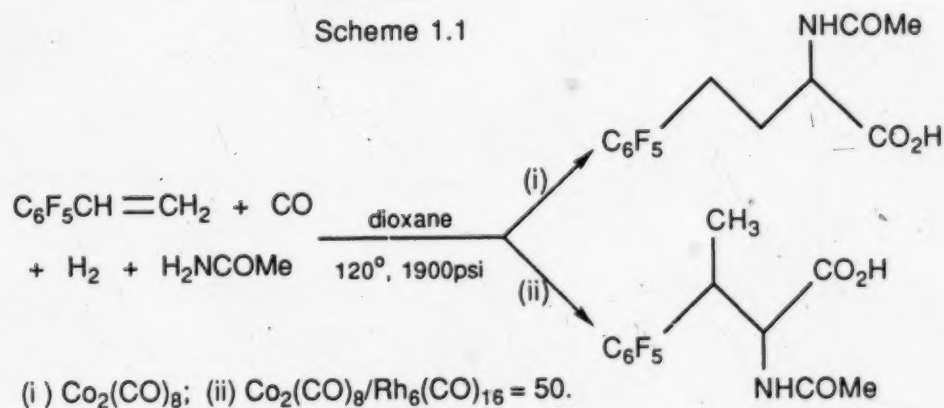


already some examples of homodinuclear compounds which are active in catalytic cycles. For example, dinuclear Rh complexes act as homogenous catalysts for the hydrogenation and hydroformylation of olefins, and the hydrogenation and cyclotrimerization of alkynes⁴. A further benefit of studying dinuclear compounds is that the new chemistry discovered may have applications in organic synthesis⁵.

A logical extension of the work centred on homodinuclear compounds is to study the chemistry of heterodinuclear compounds. Heteronuclear (or mixed metal) compounds are particularly interesting as a result of potentially combining the different reactivity properties of the constituent metals. In addition, the nature of the products may provide clues to the adopted reaction pathways, and hence to the role played by the individual metals. Therefore, these complexes are potentially very useful for catalysis, or for modelling catalytic reactions, since every catalytic transformation involves a number of steps and it is unlikely that the maximum selectivity and yield for each step will be obtained from one individual metal⁶.

One recent example of a mixed-metal system which proved to have different properties than the constituent homometallic systems is provided by the $\text{Co}_2(\text{CO})_8/\text{Rh}_6(\text{CO})_{16}$ catalysed hydroformylation-amidocarbonylation of pentafluorostyrene (PFS)⁷ (Scheme 1.1):

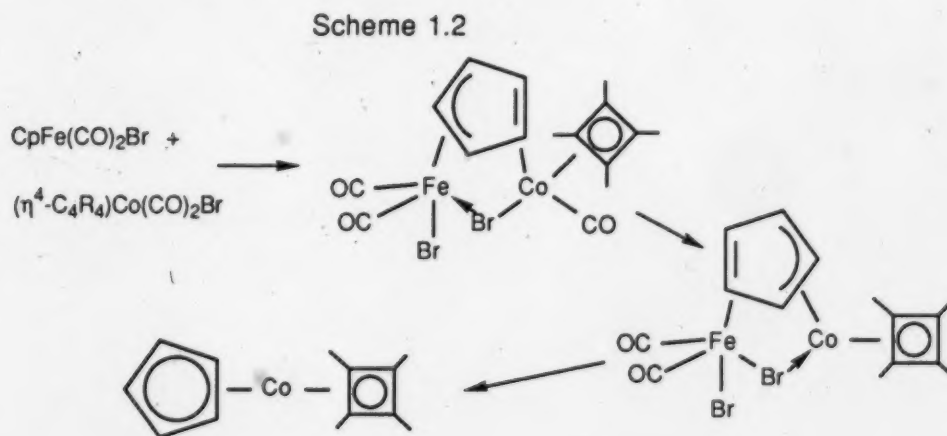
Scheme 1.1



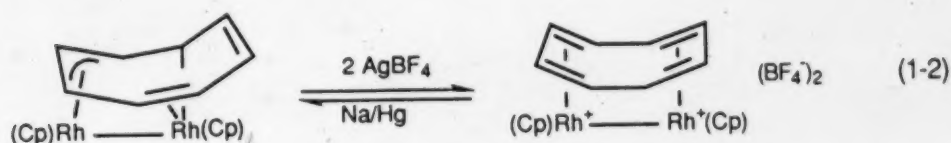
The hydroformylation-amidocarbonylation of PFS using $\text{Co}_2(\text{CO})_8/\text{Rh}_6(\text{CO})_{16}$ led predominantly to the branched chain product (path ii) with 80 % regioselectivity. In contrast, $\text{Co}_2(\text{CO})_8$ catalysis led to the straight chain product (path i) with 90 % regioselectivity. In the mixed-metal system it was determined that the unsaturated heterodinuclear complex $\text{CoRh}(\text{CO})_7$ is an active species in the formation of the branched chain product⁷.

1.2. Bimetallic Compounds containing Cyclic Polyolefinic Bridging Ligands.

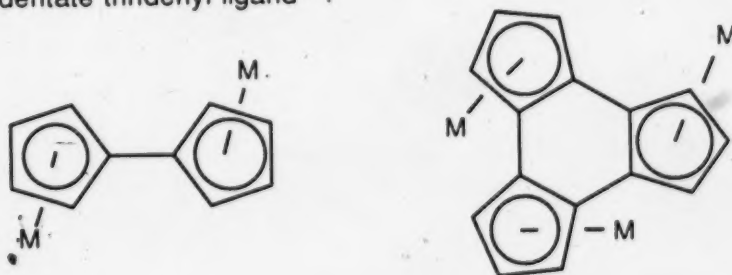
There are several benefits to a polyolefinic bridging-ligand system. In addition to holding the two metals in close proximity to one another as a reaction proceeds, polyolefin type bridging units also have the ability to create sites of unsaturation by allowing ring slippage to occur⁸. This property, when combined with rearrangement of the remaining ligands can lead to a variety of possible coordination modes. Hence, the incipient coordinative unsaturation allows associative reaction pathways to occur, and the variable coordination modes accessible to the polyolefinic ligand thus allows a myriad of different reaction pathways. The extreme case of an olefinic bridging ligand changing bonding mode between two metals is provided by complete transfer of a cyclopentadienyl ligand from Fe to Co⁹. The proposed mechanism is shown below.



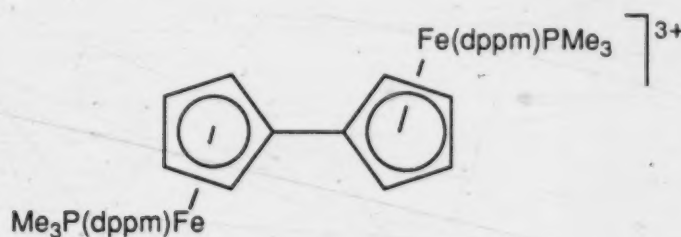
Clearly, depending on the ligand system adopted and the transition metal complexes used a variety of different structural types can be obtained. An interesting example of a bridging ligand adapting its bonding mode to suit the electronic requirements of the two coordinated metals is provided by the redox behaviour of the bis(cyclopentadienyl rhodium) cyclooctatetraene complex¹⁰:



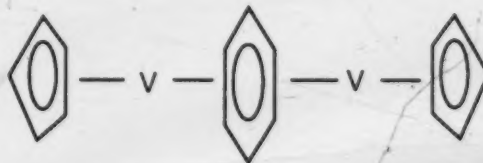
In addition to cyclooctatetraene, there are examples known of dinuclear complexes bridged by cycloheptatrienyl (*vide infra*), benzene¹¹, and cyclopentadienyl¹² ligands. Ligands which contain more than one unsaturated ring system, either fused¹³ or linked by one¹⁴ or more¹⁵ methylene units are also known. The fulvalene (Fv) ligand system which contains two cyclopentadienyl ligands linked by a C-C bond has been studied by several groups¹⁶, and is shown below. One of the more complicated ligand systems being studied which is related to fulvalene is the tridentate trindenyl ligand¹⁷:



A further useful property of polyolefinic ligands is the ability to stabilise complexes that are coordinatively unsaturated or contain an odd number of electrons^{8c,16a-d,18}. This is particularly useful in dinuclear complexes as it enables complexes of mixed oxidation states to be prepared. One example of this is provided by the fulvalene complex, $\text{Fe}_2(\text{Fv})(\text{dppm})_2(\text{PMe}_3)_2^{3+}$ (dppm = bis(diphenylphosphino)methane), which exists as a delocalised mixed valence compound^{16a}.

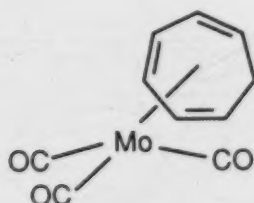


The ability to bind transition metals in a trans fashion where the two metals occupy opposite faces of the ligand is also useful as it affords possible synthetic routes to triple-decker complexes and organometallic polymers^{13c,16e,19}. An interesting example of a symmetrical triple decker complex which contains only cyclic hydrocarbon ligands is the vanadium benzene complex shown below^{12g}.

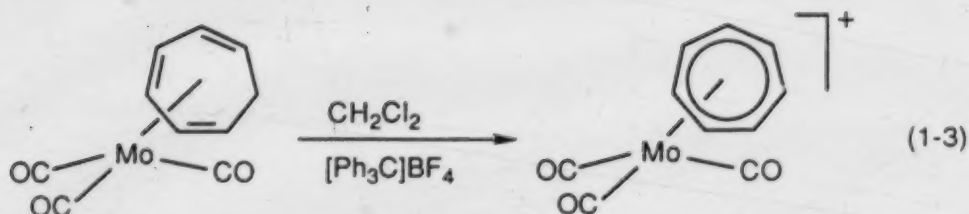


1.3. The Cycloheptatriene (C_7H_8) and Cycloheptatrienyl (C_7H_7) Ligand System.

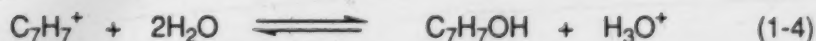
The first cycloheptatriene metal complex²⁰, $(\eta^6-C_7H_8)Mo(CO)_3$ was prepared in 1958 at a time when organometallic chemistry was in its infancy but undergoing a very rapid development²¹.



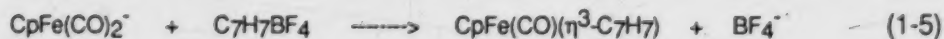
Since that time, a very large number of olefinic and polyolefinic transition metal complexes have been synthesised and studied²². Within this category of compounds, although not as widely studied as the cyclopentadienyl ligand²³, cycloheptatriene and related ligands now have an extensive and varied story of their own²⁴. Apart from the η^6 coordination mode observed in $(\eta^6-C_7H_8)Mo(CO)_3$, cycloheptatriene (CHT) is known to coordinate to single metal centres in η^4 and η^2 fashions. In these bonding modes, one and two double bonds are uncoordinated respectively. In addition, cycloheptatriene complexes may be used for the preparation of cycloheptatrienyl (C_7H_7) complexes by the abstraction of a hydride ion from the coordinated cycloheptatriene ligand²⁵:



In cationic complexes such as $(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3^+$ (shown above), the C_7H_7 ligand may best be regarded as a coordinated tropylium (C_7H_7^+) ligand. Free tropylium exists in salts such as $\text{C}_7\text{H}_7^+\text{Br}^-$ which are stable solids due to the aromaticity of the seven-membered ring²⁶. However, they will react with nucleophiles such as OH^- . For instance, when dissolved in H_2O , $\text{C}_7\text{H}_7\text{Br}$ displays an acidity ($K_a = 1.8 \times 10^{-5}$) which is close to that of acetic acid²⁶.

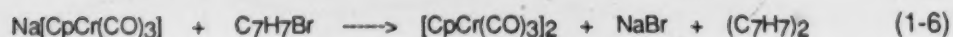


This reactivity is not always replicated in cationic transition metal complexes due to a decrease in electrophilicity of the seven-membered ring²⁷. Thus, $(\text{C}_7\text{H}_7)\text{Mo}(\text{CO})_3^+$, is much less reactive with H_2O than is free tropylium²⁷. Tropylium salts may, in some cases, be used for the direct preparation of cycloheptatrienyl transition metal compounds²⁸ (e.g. equation 1.5).

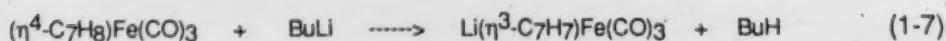


However, in many cases these reactions do not work and instead electron transfer reactions occur leading to the stable ditropyl, $(\text{C}_7\text{H}_7)_2$. Because of

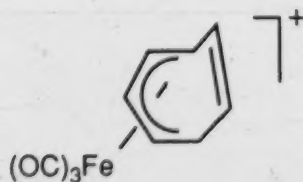
this property, tropylium bromide may be used as an oxidising agent in the preparation of $[\text{CpCr}(\text{CO})_3]_2$:²⁹



Cycloheptatrienyl transition metal complexes can also be prepared by removal of a proton from coordinated cycloheptatriene complexes:³⁰



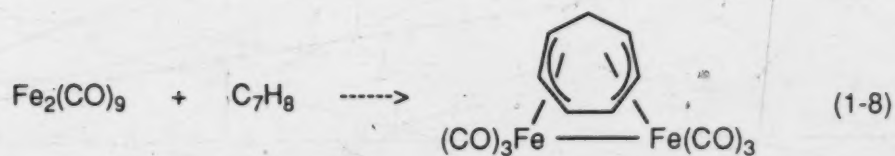
This contrasts with the known reactivity of cycloheptatriene which has proven difficult to deprotonate³¹. In fact, a satisfactory synthetic route to the cycloheptatrienide anion does not exist³¹. If one considers $(\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3^-$ to be a coordinated complex of C_7H_7^- , this then provides one of the many examples of an organic fragment being stabilised upon coordination to a transition metal centre. Interestingly a related tropylium complex, $[(\eta^5\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3][\text{BF}_4^-]$ is also known:^{27b}



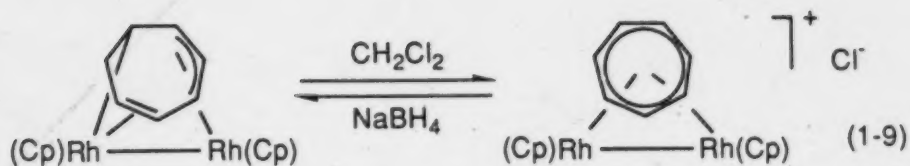
As indicated, in these examples, and in accord with the 18-electron rule³², the seven-membered ring is not attached to iron via all seven carbon atoms but is bonded in an η^3 and η^5 mode respectively. The

different bonding mode represents the ligand's ability to change its bonding mode according to the electronic requirements of the constituent parts of the molecule and to allow charge delocalization onto the transition metal centre. This charge delocalization is also demonstrated in the average carbonyl stretching frequencies of $(\eta^5\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3^+$, $(\eta^4\text{-C}_7\text{H}_8)\text{Fe}(\text{CO})_3$ and $(\eta^3\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3^-$ which are 2095, 2025 and 1905 cm^{-1} respectively. The dramatic effect on the carbonyl groups clearly demonstrates that the positive or negative charge in the ionic complexes is not solely residing upon the seven membered ring but that a modest distribution of charge occurs over the entire molecule. Apart from the η^5 and η^3 bonding modes of the C_7H_7 ligand as mentioned above, η^7 and η^1 bonding modes are also known²⁴.

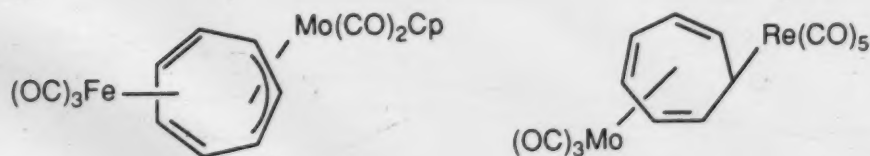
Dinuclear complexes of CHT or C_7H_7 are also known. However, the first, and still the majority of compounds of this class are homodinuclear complexes. These complexes can be prepared by reaction of the parent ligand with the respective bi- or polymetallic compound³³ (equation 1-8).



Dinuclear cycloheptatrienyl-bridged complexes may also be prepared via abstraction of a hydride from a coordinated CHT ligand. This reaction is illustrated for a dinuclear Rh complex (equation 1-9)³⁴.



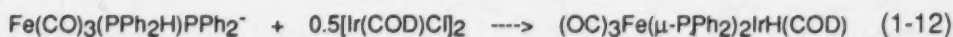
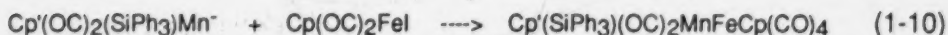
The most common coordination mode of the $\mu\text{-C}_7\text{H}_7$ ligand involves coordination of three carbon atoms to one metal centre and four carbon atoms to the second metal centre with both metals being on the same face of the ring (i.e. a $\text{cis-}\eta^3, \eta^4\text{-}$ bonding mode). Several examples of this type of coordination are mentioned in Section 1.5. Examples of dinuclear cycloheptatrienyl complexes in which two metals are on the opposite faces of the seven-membered ring in $\text{trans-}(\eta^3, \eta^4\text{-})^{35}$ or $\text{trans-}(\eta^1, \eta^6\text{-})$ coordination modes³⁶ are also known (see below).



1.4. Typical Preparations of Heterobimetallic Compounds.

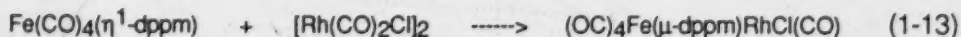
Of the wide variety of synthetic strategies used to produce heterobimetallic complexes^{6a}, one of the most commonly used involves a ligand substitution reaction at a mononuclear metal centre. This methodology includes substitution of an anionic ligand by an anionic metal complex (equation 1-10)³⁷, addition reactions, [where a second

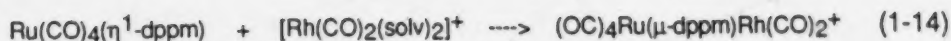
neutral metal can take the role of a ligand (equation 1-11)]³⁸, and bridge assisted substitution reactions (equation 1-12)³⁹.



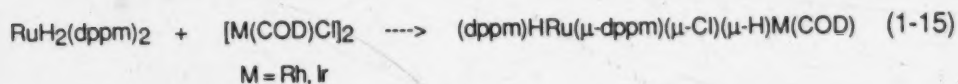
In this last strategy a bi- or poly-dentate ligand initially coordinated to only one metal is used to form a bridge in the reaction. The most commonly used bridging ligands are polyphosphines, however the method also works for other ligands including polyolefinic compounds.

One ligand that has played an extensive role in the development of the chemistry of bridged dinuclear complexes is the bridging diphosphine ligand, bis(diphenylphosphino)methane (dppm)⁴⁰. Recently this ligand has also been utilised for the preparation of heterobimetallic compounds. In this effort, the mononuclear iron compound, $\text{Fe}(\text{CO})_4(\eta^1\text{-dppm})$ has been used for the preparation of many bimetallic compounds including $(\text{OC})_4\text{Fe}(\mu\text{-dppm})\text{RhCl}(\text{CO})$ ⁴¹ (equation 1-13). In our group, the mononuclear compound $\text{Ru}(\text{CO})_4(\eta^1\text{-dppm})$ has recently been prepared, and its reaction with $[\text{Rh}(\text{CO})_2(\text{solv})_2]^+$ has also been reported⁴².



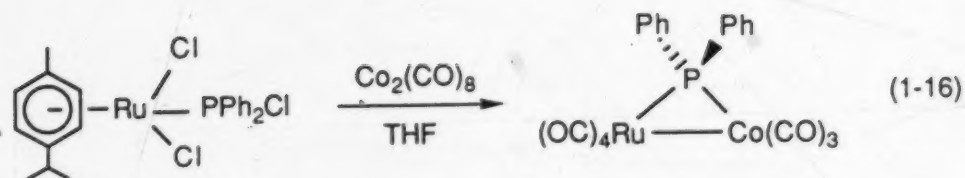


In related work, Poilblanc has used $\text{RuH}_2(\text{dppm})_2$ as a starting material for the synthesis of heterobimetallic compounds. Reaction with $[\text{Rh(COD)Cl}]_2$ and $[\text{Ir(COD)Cl}]_2$ yielded dinuclear compounds containing bridging and chelating dppm ligands⁴³ (equation 1-15). A similar chelate ring opening



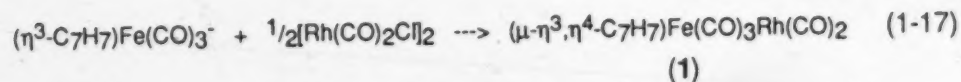
was seen in the reaction of $\text{OsCl}_2(\text{dppm})_2$ with $[\text{Rh(CO)}_2\text{Cl}]_2$ ⁴⁴ to give $\text{Cl}_2\text{Os}(\mu\text{-CO})_2(\mu\text{-dppm})_2\text{RhCl}$. These reactions are surprising due to the general inertness of octahedrally coordinated bis dppm complexes of d^6 transition metals⁴⁴ and presumably reflect the thermodynamic driving force of the reaction.

A different phosphorous containing ligand that is commonly used to bridge metal-metal bonds is the phosphido group^{6a,39}. In similar fashion to polyolefinic species, this ligand has the ability to adjust its coordination mode as it donates one electron to one metal in a P-M σ -bond and donates two electrons from the lone pair of electrons on P to the second metal in a dative fashion. In one unusual reaction, Dixneuf prepared a dinuclear RuCo complex in 35 % yield⁴⁵ (equation 1-16):



1.5. Cycloheptatrienyl Bridged Heterobimetallic Complexes and Scope of the Present Research.

A synthetic route for preparing *cis*-(μ - η^3, η^4 -C₇H₇) bridged heterobimetallic complexes has been developed in this group⁴⁶. The initial route to these complexes involved utilization of (η^3 -C₇H₇)Fe(CO)₃⁻ and its reaction with transition metal carbonyl halide complexes such as [Rh(CO)₂Cl]₂^{46a}.



This has led to the preparation of a series of metal-metal bonded complexes, (μ - η^3, η^4 -C₇H₇)Fe(CO)₃M'(CO)_n, (M' = Rh, Ir, Mn, Re)^{40a-c} and also more recently, through the use of (η^3 -C₇H₇)Ru(CO)₃⁻ and [Rh(COD)Cl]₂, to (μ - η^3, η^4 -C₇H₇)Ru(CO)₃Rh(COD)^{46d}. It was found that the best reactants for the production of these heterobimetallic complexes were the Rh and Ir cyclooctadiene complexes, [M(COD)Cl]₂, with the best yield (65%) being for the FeRh combination. Preparation of the FeRh cyclooctadiene complex has also been reported independently by Salzer³⁴, who noted that the ⁵³Fe and ¹⁰³Rh NMR indicated that the

anionic nature of the Fe centre, and cationic nature of the Rh centre in the starting materials was maintained in the product. The initially produced cyclooctadiene complexes react with CO in hydrocarbon solvents to give the corresponding pentacarbonyl complexes in almost quantitative yield (as shown for the RuRh complex):



Elementary reactivity studies on the FeRh and RuRh pentacarbonyl complexes, **1** and **2**, showed that rapid phosphine substitution reactions occur at the Rh centre^{46b,d}. This and the observed carbonyl scrambling processes known to occur have been attributed to the variable coordination mode of the seven-membered ring and the attendant incipient coordinative unsaturation at the metal centres. Further support for this suggestion came when the reaction of the RuRh pentacarbonyl complex, **2**, with dppm was monitored by low temperature ³¹P NMR and gave evidence for intermediates where ring slippage has occurred^{8b}. The ultimate product in this reaction was a bridging compound caused by substitution of one carbonyl group on each metal (equation 1-19).



An extension of these studies has been provided by Salzer who found that reaction of $(\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3^-$ with $[(\text{allyl})\text{PdCl}]_2$ and

$[(2\text{-methylallyl})\text{PdCl}]_2$ afforded fluxional iron-palladium complexes. In the same fashion, $(\text{C}_7\text{H}_7)\text{Co}(\text{CO})_3$ (which is isoelectronic to the Fe anion) reacts with $\text{Rh}(\text{NBD})^+$ to give a cycloheptatrienyl bridged cationic CoRh complex⁴¹.

In continuation of these studies and described in this thesis, the related ruthenium-iridium complex, *cis*-($\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7$) $\text{Ru}(\text{CO})_3\text{Ir}(\text{COD})$ (**3**) has been prepared, and the reactivity of the RuRh and RuIr complexes, **2** and **3** with alkynes has been investigated. Additionally, the synthesis and characterization of the anionic complex $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ has been accomplished and its reactivity with $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M}' = \text{Rh}, \text{Ir}$) studied. Surprisingly, the reactivity was different from that of the analogous Fe and Ru anionic complexes. This led to the synthesis and spectroscopic characterization of isomeric *cis* and *trans* cycloheptatrienyl bridged OsRh complexes, and of *cis*-($\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7$) $\text{Os}(\text{CO})_3\text{Ir}(\text{COD})$. Comparisons of the spectroscopic properties of the *cis* heterobimetallic compounds $(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{COD})$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}; \text{M}' = \text{Rh}, \text{Ir}$) and of the precursor anionic complexes $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) are also presented.

1.6. References.

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Chapter 2.

Synthesis, Properties, and Reactivity of *cis*- (μ -C₇H₇)Ru(CO)₃Ir(L₂) (L₂ = COD, L = CO). Preparation and Fluxional Behaviour of *cis*-(μ -C₇H₇)Ru(CO)₃Ir(CO)PPh₃.

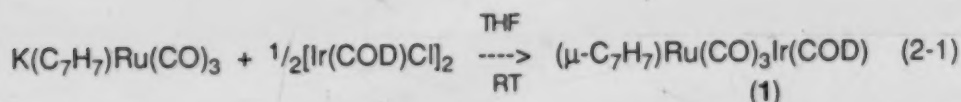
2.1. Introduction.

As already mentioned in Chapter 1, previous studies in the Takats' group has involved the preparation and investigation of the chemical properties of *cis* cycloheptatrienyl-bridged heterobimetallic carbonyl complexes of FeRh², RuRh³, and FeIr⁴. As a result of these studies, it has been suggested that the variable bonding capacity, and the incipient coordinative unsaturation of the cycloheptatrienyl ring are responsible for facile CO substitution and carbonyl scrambling processes in these complexes. In this chapter, in an extension of these studies, the preparation and spectroscopic characterization of *cis*-(μ -C₇H₇)Ru(CO)₃Ir(L₂) [L₂ = COD (1), L = CO (2)] (COD = 1,5 cyclooctadiene) are described. Substitution reactions of 2 to give fluxional bimetallic complexes which contain a single phosphine ligand are also reported. The spectroscopic effects of replacing a ligand on the bimetallic unit are discussed, and comparisons with the analogous complexes of FeRh², RuRh³, and FeIr⁴ are made when available.

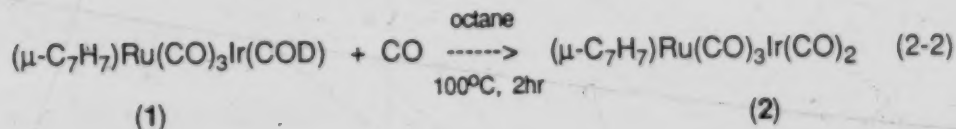
2.2. Results and Discussion

2.2.1. Preparation of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{COD})$ (1) and $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (2).

Addition of $\text{K}(\text{C}_7\text{H}_7)\text{Ru}(\text{CO})_3$ to $[\text{Ir}(1,5\text{-cyclooctadiene})\text{Cl}]_2$ in THF at room temperature, followed by stirring for 12 hours gives a very dark brown solution. Removal of the solvent and extraction in hexane affords $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{COD})$ (1, equation 2-1) as the only observed product.



Chromatographic work up leads to the isolation of complex 1 in 23% yield as yellow, air stable crystals which are freely soluble in common organic solvents. The IR spectrum displays a three band pattern consistent with three carbonyl groups occupying terminal positions on Ru. Whilst the yield of 1 is poor, it is similar to that observed (30 %) for the analogous RuRh complex prepared under similar conditions⁵. On reaction with CO at 100 °C, 1 is quantitatively converted to $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (2) over a two hour period (equation 2-2).



The same thermal conditions (100 °C, 1 atm CO) were required for preparation of the related FeIr complex, $(\mu\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3\text{Ir}(\text{CO})_2$. These

conditions are significantly more forcing than those required for the carbonylation of the analogous FeRh and RuRh cyclooctadiene complexes, which are both carbonylated in less than an hour at room temperature. Complex **2** is a yellow-orange air stable and thermally robust solid, also soluble in most organic solvents. The IR spectrum shows five peaks in the terminal carbonyl region as has been previously observed for the related FeRh, FeIr, and RuRh complexes.

As expected, the ^1H and ^{13}C NMR data for **1** and **2** give evidence for rapid ring whizzing of the cycloheptatrienyl ligand at ambient temperature. However, as can be seen in Figure 2.1, rotation of the COD ligand in **1** is not observed, there being two sharp resonances for the olefinic hydrogens and carbons in the ^1H and ^{13}C NMR spectra respectively. A similar observation was made in the corresponding FeIr compound⁴, but in the analogous RuRh complex⁵ rotation of the COD ligand occurs as evidenced by the single olefinic resonance in the room temperature ^1H NMR spectrum. This reflects the well known decrease in metal to ligand bond strength upon ascending a transition metal triad⁶. The observation that the RuIr pentacarbonyl complex, **2**, requires temperatures of 70 °C to give complete enrichment with ^{13}CO is also consistent with this trend. Surprisingly, the variable temperature ^1H NMR spectra of **1** and **2** indicate that the rotation of the $\mu\text{-C}_7\text{H}_7$ ligand can be frozen out. As shown in Figures 2.2 and 2.3, the low temperature limiting spectra are approached at -100 °C for both complexes. Assignments of the resonances were made by comparison with the related OsIr complexes (Chapter 4) which

Figure 2.1. ^{13}C (a) and ^1H (b) NMR spectra of 1 in the C_7H_7 and COD region.

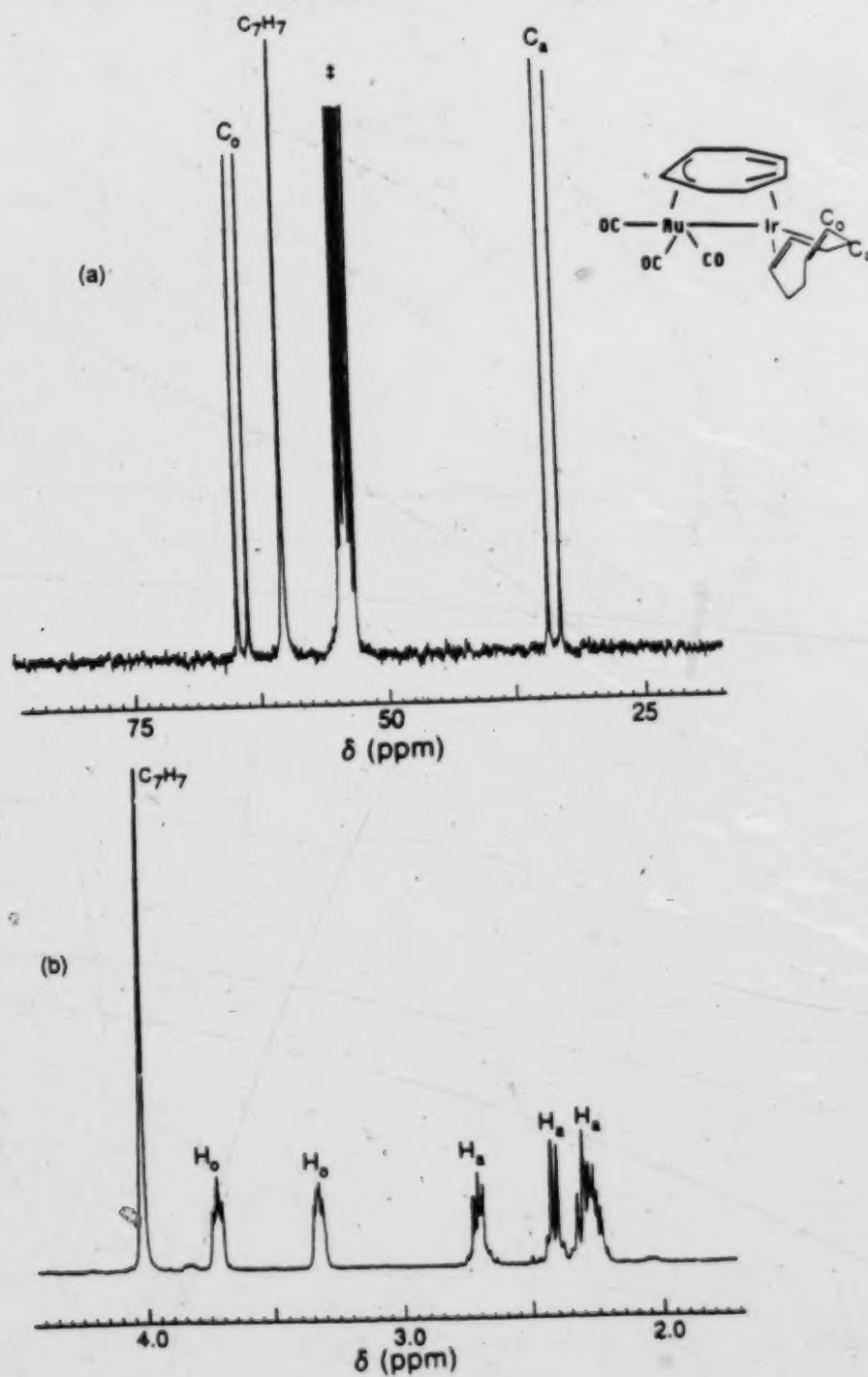


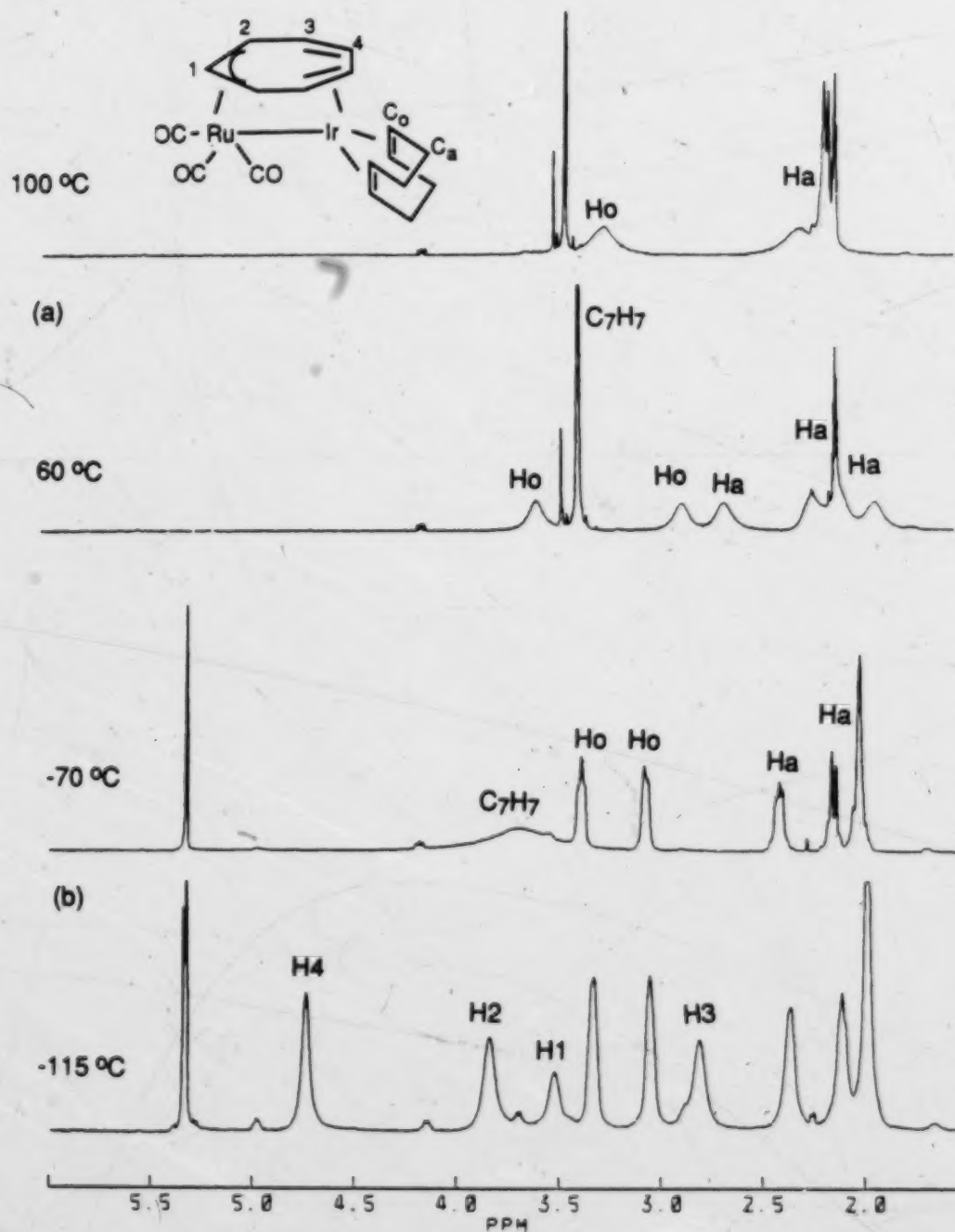
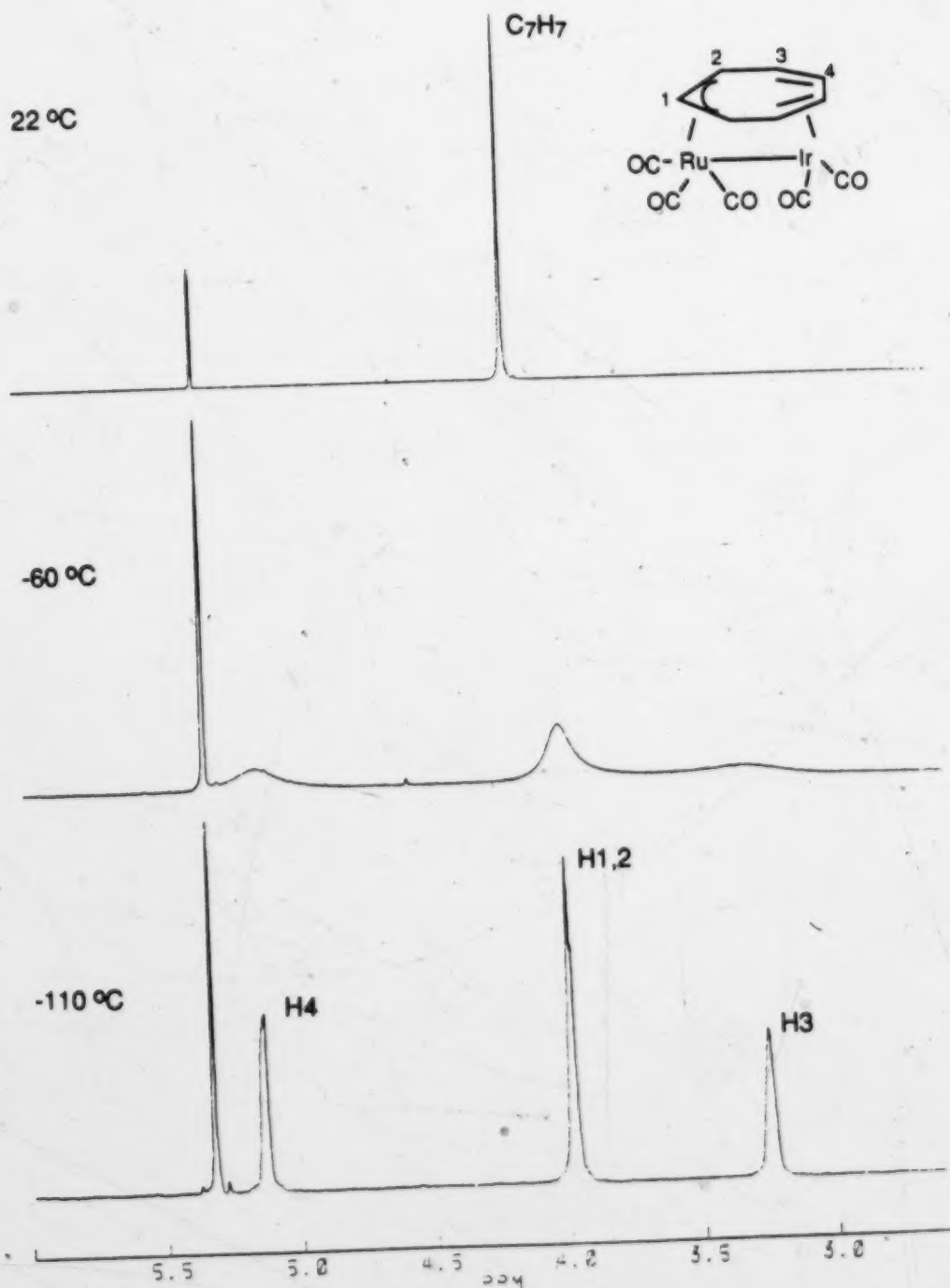
Figure 2.2. Variable Temperature ^1H NMR Spectra of 1.(a) Spectra recorded in toluene- d_8 . (b) Spectra recorded in CD_2Cl_2 .

Figure 2.3. Variable Temperature ^1H NMR Spectra of 2.

have been determined by a series of decoupling experiments. Another noteworthy observation is that high temperature ^1H NMR spectra of the RuIr cyclooctadiene complex, **1**, (60 $^\circ\text{C}$, 100 $^\circ\text{C}$, Figure 2.2) give evidence for rotation of the COD ligand. The fluxional processes involving the COD and C_7H_7 ligand, and complementary results in related Os complexes, will be commented upon more fully in Chapter 4 and in Chapter 7.

In their ^{13}C NMR spectra, both complexes **1** and **2** display a sharp singlet for the three CO ligands on Ru due to rapid scrambling of the CO groups on one metal centre. Intermetallic CO exchange is not observed in **2** at ambient temperature; there being two sharp resonances at δ 196 ppm (CO_{Ru}) and δ 175 ppm (CO_{Ir}), easily distinguishable on the basis of their chemical shifts⁷. These signals remain sharp until 70 $^\circ\text{C}$ when slight broadening is noticed. Coalescence of the two signals was not observed upon heating an NMR sample of **2** in dodecane/toluene- d^8 (ca. 10:1) to 120 $^\circ\text{C}$. At these temperatures some decomposition of the sample occurs. Intermetallic CO scrambling was also not observed at elevated temperatures for the analogous FeRh , FeIr , and RuRh pentacarbonyl complexes. The variable temperature ^{13}C NMR spectra of the pentacarbonyl complex **2** are shown in Figure 2.4. Although heating **2** failed to give evidence of global carbonyl scrambling, the low temperature NMR spectrum recorded at -80 $^\circ\text{C}$ (Figure 2.4) showed halting of the local carbonyl scrambling at the Ru centre. Thus two signals for the $\text{Ru}(\text{CO})_3$ carbonyls are observed at δ 199.9 (2C) and δ 189.3 (1C). Of course, at

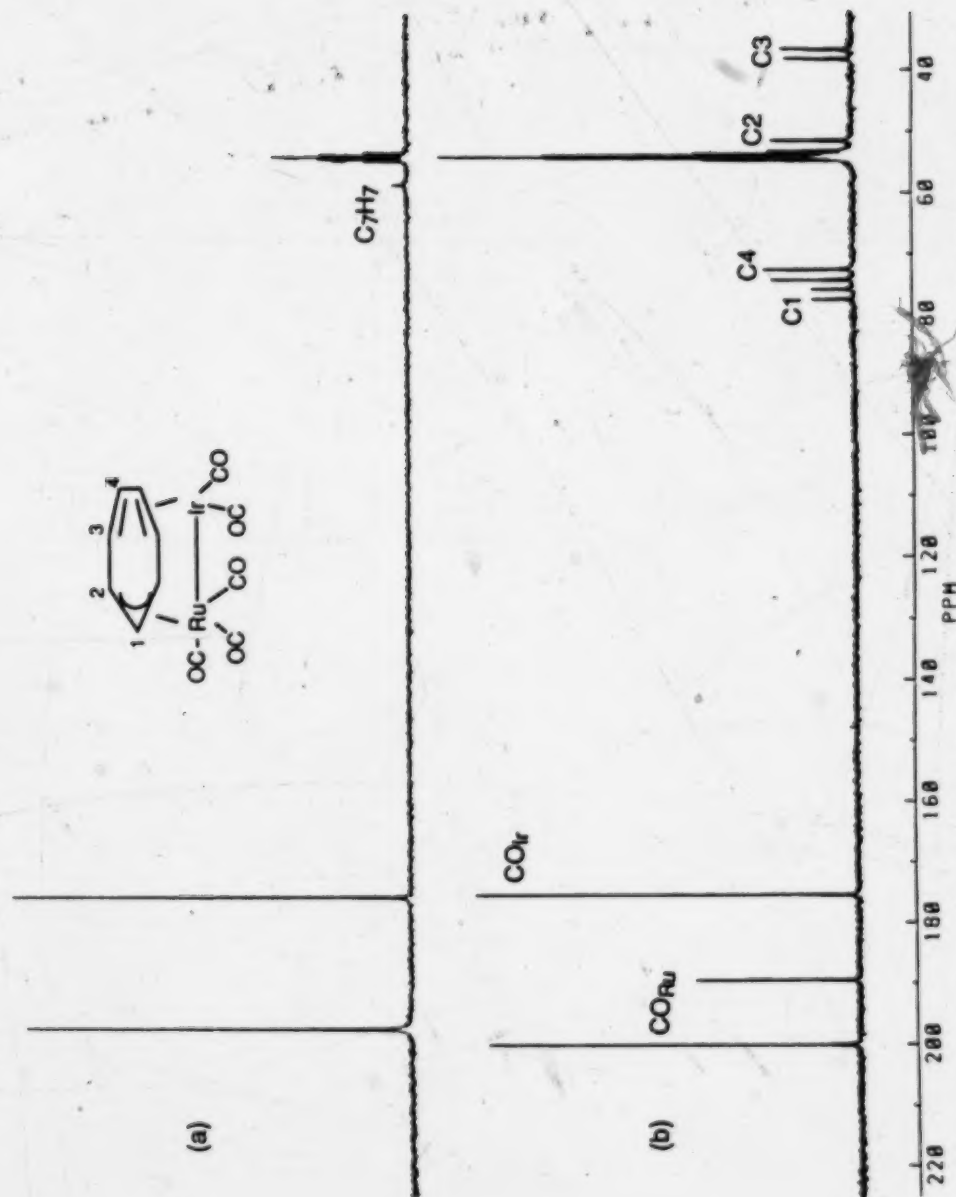


Figure 2.4. (a) Room Temperature (^1H) ^{13}C NMR Spectrum of 2 (enriched with ^{13}CO).

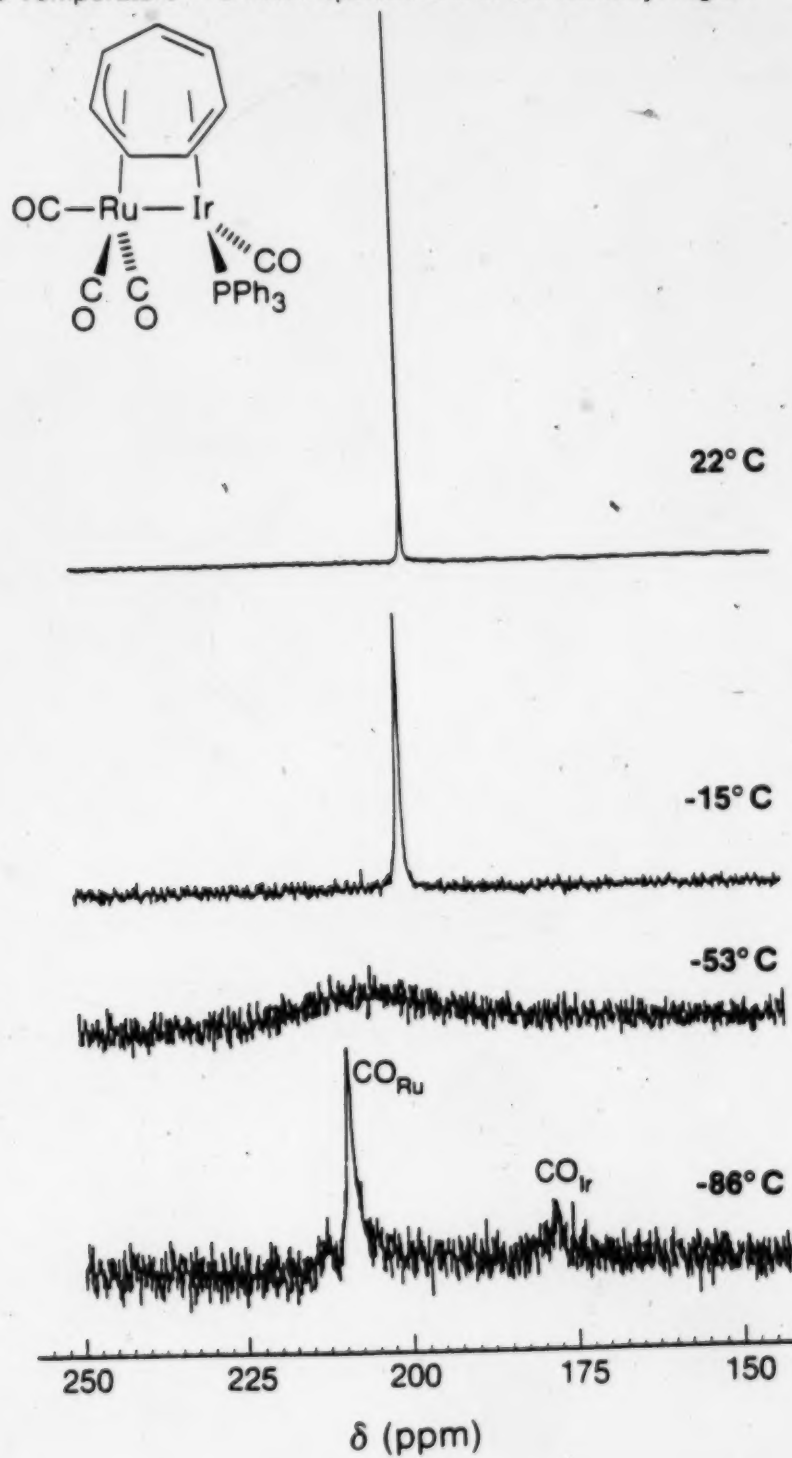
(b) Low Temperature (proton coupled) ^{13}C NMR of 2 (^{13}CO in natural abundance).

this temperature the rotation of the seven-membered ring is also frozen out.

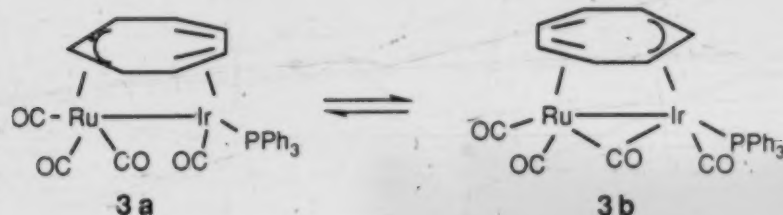
2.2.2. Preparation of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})(\text{PPh}_3)$ (**3**).

Although the carbonylation experiments had required thermal activation, it was observed that **2** reacted with one equivalent of PPh_3 cleanly at room temperature giving substitution of one CO ligand. The ^{31}P NMR spectrum of the product shows one singlet at δ 5.2 ppm. The variable temperature ^{13}C NMR spectra are shown in Figure 2.5. The ^{13}C NMR spectrum in the carbonyl region displays one sharp singlet at room temperature indicating rapid intermetallic CO exchange. As seen in Figure 2.5, upon decreasing the temperature the signal broadens and coalescence is observed at -53°C . At -85°C intermetallic CO exchange is not completely frozen out, however, it can be seen that there are two resonances at δ 210 ppm and δ 179 ppm in a 3:1 ratio. These signals therefore indicate that phosphine substitution has occurred at Ir and that at -85°C , there is local carbonyl scrambling within the $\text{Ru}(\text{CO})_3$ group. At this temperature there is also one signal for the C_7H_7 ligand indicating that the seven-membered ring is also involved in a form of fluxional behaviour. Both of these processes are close to being frozen out at this temperature for **1** and **2**, indicating that the presence of PPh_3 significantly enhances the fluxional behaviour of the bimetallic complexes. The site of attack in the formation of **3** is presumably determined by the more pronounced tendency of Ir to produce 16 electron species via ring dissociation⁸.

Figure 2.5.

Variable Temperature ^{13}C NMR Spectra of **3** in the carbonyl region.

The IR spectrum of compound **3** is complicated due to the presence of both all terminal, (**3a**) and carbonyl bridged (**3b**) isomers, as has been previously noticed in the related FeRh^2 and FeIr^4 complexes. The isomerization involves a change in the bonding mode of the ($\mu\text{-C}_7\text{H}_7$) moiety between the two metals as shown below. Rapid equilibrium



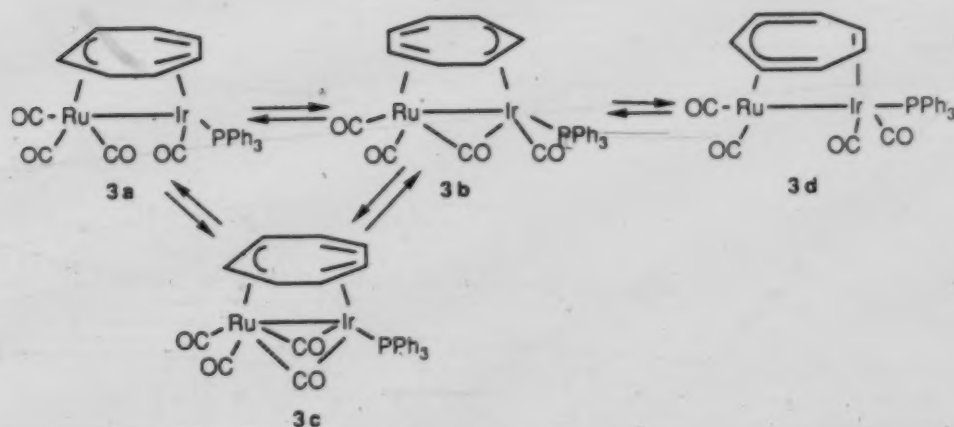
between these isomers would lead to interchange of carbonyl groups on Ru and hence explains the low temperature ^{13}C NMR spectrum. Clearly there is a very low activation energy for this process.

The free energy of activation for intermetallic carbonyl exchange in **3** calculated at the coalescence temperature⁹ is 9.0 kcal/mole. This can be compared with the analogous complexes of RuRh (11.0 kcal/mole), FeIr (10.3 kcal/mole) and FeRh (15.4 kcal/mole). Of the several plausible intermediates available for this process, we have previously favoured the doubly bridged species **3c** (Scheme 2.1). The rationale behind our choice was that **3c** is easily achieved from both isomeric **3a** and **3b** while maintaining the $\mu\text{-}\eta^4, \eta^3$ bonding functionality of the cycloheptatrienyl ring. However the surprising and unexpected trend of increasing facility for carbonyl group migration ($\text{Ru} > \text{Fe}$ and $\text{Ir} > \text{Rh}$) is difficult to reconcile with this postulate since it is contrary to the well known greater reluctance of

transition metals to accommodate bridging carbonyl groups upon descending a triad¹⁰.

It now seems possible that an alternative intermediate (**3d**) which contains only terminal carbonyl ligands may also be involved in this process and may gain importance upon descending a triad. The necessary change in bonding mode of the cycloheptatrienyl ring to $\mu\text{-}\eta^5, \eta^2$ may in this case dominate the energetics for global carbonyl scrambling, and account for the observed trend.

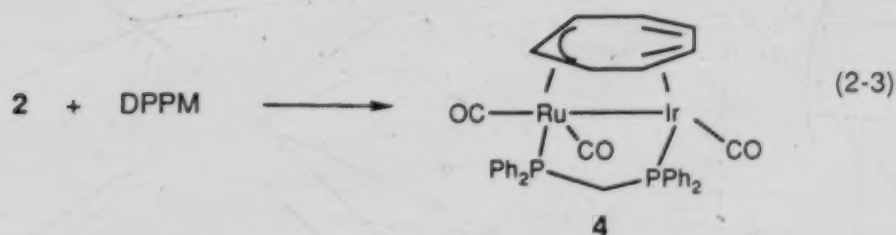
Scheme 2.1



2.2.3. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ with dppm.

The reaction of **2** with bis(diphenylphosphino)methane (dppm) was carried out under conditions similar to the reaction with PPh_3 , but this time the displacement of two CO groups was observed. The IR spectrum of the product shows three bands, all in the terminal carbonyl stretching region at

1980, 1936, and 1914 cm^{-1} . Two doublets were observed in the ^{31}P NMR spectrum at δ 65.3 ppm (Ru) and δ 25.0 ppm (Ir) with P-P coupling constants of 125 Hz, typical of μ -dppm complexes¹¹. The ^{13}C NMR in the carbonyl region now shows three resonances at room temperature at δ 208 ppm (Ru), δ 196 ppm (Ru) and δ 183 ppm (Ir).



These data are characteristic^{2,3} of the expected product $(\mu\text{-C}_7\text{H}_7)(\mu\text{-DPPM})\text{Ru}(\text{CO})_2\text{Ir}(\text{CO})$, **4**. The reaction was followed at room temperature by IR and ^{31}P NMR spectroscopies, but these studies failed to give evidence for any intermediates. A reasonable explanation for this would be that the reaction proceeds via slow initial substitution at Ir, in a fashion similar to the PPh_3 reaction and this is followed by rapid substitution of a second carbonyl group at Ru leading to product formation (i.e. the chelate effect¹²). Unfortunately, crystallization failed to eliminate various phosphorus containing minor impurities which appeared erratically in the ^{31}P NMR spectrum. In addition, **4** appears less thermally stable and is considerably more air sensitive than **3**, which renders purification more difficult. The decrease in stability upon addition of phosphorus donor ligands is probably electronic in origin and perhaps opens new channels for competing reaction pathways leading to the unexpected minor

byproducts. Due to these difficulties, complex 4 was not further investigated.

2.3. Conclusion.

The synthesis of the series of complexes $(\mu\text{-C}_7\text{H}_7)\text{MM}'(\text{CO})_4\text{L}$ ($\text{M}=\text{Fe}, \text{Ru}$ and $\text{M}'=\text{Rh}, \text{Ir}$; $\text{L}=\text{CO}, \text{PPh}_3$) has been completed. For $\text{L}=\text{PPh}_3$ a decrease in activation energy for intermetallic CO exchange is noticed on going from Fe to Ru and from Rh to Ir. Due to the necessary involvement of bridging carbonyl groups in this process, this is a surprising result in view of the greater tendency to accommodate bridging carbonyls for 1st row transition metals. It has however been noticed that substitution by phosphines increases the tendency for carbonyl groups to occupy bridging positions, and also the facility for carbonyl group migration¹³. This effect is dramatically demonstrated in our observation that intermetallic CO scrambling is facile for the phosphine complex 3, but it is not observed in the pentacarbonyl complex 2.

2.4. Experimental.

2.4.1. General Techniques.

Reactions and manipulations were carried out under purified nitrogen using standard Schlenk and canula techniques¹⁴ and carefully dried solvents. N₂ was purified by passage through a heated column (100 °C), containing BASF (Cu-based) catalyst R3-11 to remove oxygen and a column of Malinkrodt Aquasorb (P₂O₅ on an inert base) to remove water. Solvents were dried by refluxing and distilling from the appropriate drying agent under N₂ (Table 2.1).

Table 2.1 Drying Agents used in the Distillation of Solvents.

Solvent	Drying Agent
Pentane	CaH ₂
Hexane	Potassium metal
Benzene	Potassium metal
Toluene	Sodium metal
THF	Potassium metal/benzophenone
CH ₂ Cl ₂	P ₂ O ₅ .

Pentane and hexane were preconditioned before refluxing and distillation by washing with H₂SO₄ and water and drying over Na₂SO₄ in order to remove alkenes. All deuterated solvents were dried over molecular sieves except THF-*d*₈ which was distilled from Na-

benzophenone prior to use. Glassware was cleaned by treatment with KOH-ethanol solution and was oven-dried at 100 °C. Separation and purification of compounds was done by crystallization or by silica gel column chromatography (using Merck Kieselgel 60 PF₂₅₄ silica gel) unless otherwise stated.

2.4.2. Physical Measurements.

Reactions were monitored by infrared spectroscopy with the aid of a Nicolet MX-1 Fourier Transform Interferometer over the range 2200 - 1600 cm⁻¹. Solution samples were held between KBr or KCl (0.1 mm) plates. Mass spectra and NMR spectra were recorded by the staff of the respective laboratories. Mass spectra were recorded on an A.E.I. MS-12 spectrometer operating at 70 eV or 16 eV. The mass number of the molecular ion refers to the most abundant isotope combination. NMR spectra were recorded on a Bruker WH 200, Bruker AM 400 or Bruker AM 300 spectrometer. Variable temperature spectra were recorded on the Bruker AM 400 with samples which were either sealed under vacuum or by wrapping the plastic cap with parafilm. Solvent resonances (vs. TMS) were used as internal standards for ¹H and ¹³C NMR spectra. H₃PO₄ was used as a calculated external standard for ³¹P spectra (downfield being positive). Melting points were obtained on a Thomas Hoover apparatus in open capillaries and are uncorrected. Elemental analyses were performed by the Microanalytical Laboratory of this department.

2.4.3. Reagents for Chapter 2.

Bis(diphenylphosphino)methane (DPPM) was purchased from Pressure Chemical Company and triphenylphosphine, dodecane, and 1,5-cyclooctadiene (COD) from Aldrich, these materials were used as received. Ammonium hexachloroiridate (IV) was obtained from Engelhard. Potassium tertiarybutoxide (KO^tBu) was purchased from Aldrich and sublimed prior to use (150 °C, 10⁻³ mmHg). [Ir(COD)Cl]₂¹⁵ and (C₇H₈)Ru(CO)₃⁵ were prepared according to literature methods. Octane was obtained from Terochem Laboratories Ltd. and degassed by three freeze-pump-thaw cycles before use.

2.4.4. (μ-C₇H₇)Ru(CO)₃Ir(COD), (1).

K(C₇H₇)Ru(CO)₃ (4.60 mmol, 1.45 g) was prepared by the addition of equimolar quantities of KO^tBu in THF (20 ml) to (C₇H₈)Ru(CO)₃ in THF (40 ml) at -78 °C. The anion was transferred to a jacketed dropping funnel which was cooled by dry-ice and was then added dropwise to a solution of [Ir(COD)Cl]₂ (2.30 mmol, 1.54 g) in THF (40 ml) at room temperature. The dark solution was stirred for 12 hours at room temperature and evaporated to dryness. The brown residue was extracted with 2 aliquots of toluene (20 ml) and chromatographed on a 16 x 2.5 cm silica gel column (Merck, Kieselgel 60 mesh). Elution with hexane produced a large red band which was collected under nitrogen. The solvent was removed from the eluate and the residue was redissolved in hexane (20 ml) and cooled at -78 °C for 12 hours to obtain yellow crystals (0.462 g, 17%). Concentration of the mother liquor to 2ml yielded a final crop (0.140 g, 23% overall) mp 139 °C (dec).

Anal. Calcd for $C_{18}H_{19}IrO_3Ru$: C, 37.49; H, 3.32. Found: C, 37.66; H, 3.40.

Mass spectrum (70 eV, 90 °C): M^+ , $M^+ - nCO$ ($n = 1-3$).

IR (hexane): ν_{CO} 2038(s), 1977(s), 1970(s) cm^{-1} .

^1H NMR (25 °C, CD_2Cl_2): δ 3.82 (s, 7H, C_7H_7), 3.52 (m, 2H, CH_{COD}), 3.16 (m, 2H, CH_{COD}), 2.54 (m, 2H, CH_2COD), 2.24 (m, 2H, CH_2COD), 2.12 (m, 4H, CH_2COD).

(-100 °C): δ 2.80 (br, 2H, C_7H_7), 3.54 (br, 1H, C_7H_7), 3.76 (br, 2H, C_7H_7), 4.72 (br, 2H, C_7H_7).

^{13}C {1H} NMR (25 °C, CD_2Cl_2): δ 33.5 (s, CH_2COD), 34.7 (s, CH_2COD), 60.0 (s, C_7H_7), 63.4 (s, CH_{COD}), 64.4 (s, CH_{COD}), 196.8 (s, CO_{Ru}).

2.4.5. $(\mu-C_7H_7)Ru(CO)_3Ir(CO)_2$, (2).

$(\mu-C_7H_7)Ru(CO)_3Ir(COD)$ (90 mg, 0.16 mmol) was dissolved in octane (30 ml). The solution was degassed by two freeze-pump-thaw cycles. An atmosphere of CO was introduced to the reaction vessel, which was then heated at 100 °C for 2 hours and then evaporated to dryness in vacuo. The residue was redissolved in hexane (5 ml), concentrated to 0.5 ml, and then cooled to -78 °C over 12 hours to give yellow-orange crystals of 2 (72 mg, 73%) mp 126-127 °C.

Anal. Calcd for $C_{12}H_7IrO_5Ru$: C, 27.48; H, 1.35. Found: C, 27.94; H, 1.42.

Mass spectrum (70 eV, 110 °C): M^+ , $M^+ - nCO$ ($n = 1-5$).

IR (hexane) ν_{CO} : 2066(s), 2019(s), 2005(s), 1984(m), 1973(w) cm^{-1}

^1H NMR (25 °C, CD_2Cl_2): δ 4.16 (s, 7H, C_7H_7); (-100 °C): δ 3.24 (br, 2H, C_7H_7), 4.00 (br, 2H + 1H, C_7H_7), 5.24 (br, 2H, C_7H_7).

^{13}C $\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2): δ 58.4 (s, C_7H_7), 175.4 (s, CO_{Ir}), 196.8 (s, CO_{Ru}).

2.4.6. Synthesis of ^{13}CO enriched sample.

^{13}CO (99.1%) was purchased from Isotech Inc. Compound **2** was enriched in ^{13}CO by stirring an octane solution of **2** under 1 atm of ^{13}CO at 70 °C for 1 hour. The enrichment was 94% as determined from the mass spectrum of the compound.

2.4.7. $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})\text{PPh}_3$ (**3**).

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (31 mg, 0.059 mmol) was dissolved in C_6H_6 (15 ml), and the solution was degassed. PPh_3 (15.5 mg, 0.059 mmol) was added as a solid and the solution was stirred for 3 hours, and then evaporated to dryness. The orange residue was washed once with hexane and then recrystallised from CH_2Cl_2 /hexane at -78 °C to give orange red crystals of **3** (34 mg, 76%) mp 138 - 139 °C (dec).

Anal. Calcd for $\text{C}_{29}\text{H}_{22}\text{IrO}_4\text{PRu}$: C, 45.91; H, 2.92. Found: C, 45.82; H, 2.98.

Mass Spectrum (70 eV, 180 °C): M^+ , $\text{M}^+ - n\text{CO}$ ($n = 1-4$).

IR (C_6H_6) ν_{CO} : 2034(w), 2004(m), 1970(s,br), 1935(br), 1785(w,br) cm^{-1}

^1H NMR (25 °C, C_6D_6): δ 7.6 (m, 2H, Ph, o), 7.1 (m, 2H, Ph, m), 7.0 (m, 1H, Ph, p), 3.56 (s, 7H, C_7H_7).

^{13}C $\{^1\text{H}\}$ NMR (25 °C, CD_2Cl_2): δ 60.5 (s, C_7H_7), 128.6 (d, J_{P} ,

$\text{C} = 10.5\text{Hz}$, Ph, m), 130.6 (s, Ph, p), 135.6 (d, $\text{J}_{\text{P-C}} = 11.4\text{Hz}$, Ph, o), 136.0 (d, J_{P} ,

$\text{C}=40\text{Hz, Ph, ipso}$), 199.7 (s, CO, averaged); (-86 °C): δ 209.6 (s, CO_{Ru}), 179.3 (s, CO_{Ir}).

^{31}P { ^1H } NMR (25 °C, C_6D_6): δ 5.15 (s, PPh_3).

2.4.8. $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_2\text{Ir}(\text{CO})(\mu\text{-DPPM})$, (**4**).

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (25 mg, 0.048 mmol) was dissolved in toluene (15 ml) and the solution was degassed. DPPM (18.3 mg, 0.048 mmol) was added as a solid. The solution was stirred for 3 hours during which time starting material was consumed and **4** was formed as monitored by IR spectroscopy. The solution was then concentrated to 0.5 ml and layered with hexane (2 ml). The vessel was then cooled at -78 °C to give a bright orange air sensitive solid, **4** which was analysed immediately by NMR spectroscopy mp 75 °C (dec).

Anal. Calcd for $\text{C}_{35}\text{H}_{29}\text{IrO}_3\text{P}_2\text{Ru}$: C, 49.29; H, 3.43. Found: C, 47.88; H, 3.86.

Mass Spectrum (70 eV, 200 °C): M^+ , $\text{M}^+ - n\text{CO}$, ($n = 1-3$).

IR (benzene) ν_{CO} : 1980(s), 1936(s), 1914(m) cm^{-1} .

^1H NMR (25 °C, C_6D_6): δ 7.7-6.8 (m, 20H, Ph), 3.82 (dt, 1H, $J_{\text{H-H}}=14\text{Hz}$, $J_{\text{H-P}}=12\text{Hz}$, CH_2), 3.65 (s, 7H, C_7H_7), 2.11 (dt, 1H, $J_{\text{H-H}}=14\text{Hz}$, $J_{\text{H-P}}=8\text{Hz}$, CH_2).

^{13}C { ^1H } NMR (25 °C, toluene d_8): δ 208.2 (s, CO_{Ru}), 195.7 (d, $J_{\text{P-C}}=9\text{Hz}$, CO_{Ru}), 182.7 (d, $J_{\text{P-C}}=9\text{Hz}$, CO_{Ir}), 138.2-129.3 (Ph), 57.2 (C_7H_7), 42.2 (dd, $J_{\text{H-P}}=24, 41\text{Hz}$, CH_2).

^{31}P { ^1H } NMR (25 °C, C_6D_6): δ 65.3 (d, $J_{\text{P-P}}=125\text{Hz}$, Ru-P), 25.0 (d, $J_{\text{P-P}}=125\text{Hz}$, Ir-P).

2.5. References.

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Chapter 3.

Preparation, properties and reactivity of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$. Synthesis of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ and $(\eta^5\text{-C}_7\text{H}_9)\text{Os}(\text{CO})_2[\text{C}(\text{O})\text{Bu}]$.

3.1. Introduction.

Complexes of formula (diene) $\text{Fe}(\text{CO})_3$ compose one of the earliest studied family of transition metal organometallic complexes¹, and twenty five years later many applications of these compounds are still being studied². It is therefore not surprising that the synthesis and some properties of the $(\eta^4\text{-cycloheptatriene})\text{M}(\text{CO})_3$ complexes ($\text{M} = \text{Fe}$; **1a**, Ru ; **1b**) have for a long time been known³.

The synthesis of these compounds can be achieved by either thermal, or photochemical reaction of the appropriate binary metal carbonyl complex with cycloheptatriene, or by substitution of a labile ligand in a $\text{LM}(\text{CO})_3$ complex such as $(\text{BDA})\text{Fe}(\text{CO})_3$ or $(\text{COD})\text{Ru}(\text{CO})_3$ ($\text{BDA} =$ benzylidene acetone, $\text{COD} = 1,5$ cyclooctadiene)³. In our studies here, we have found the photochemical route to the Ru complex the most convenient⁴, and hence a similar approach was used for the synthesis of the corresponding Os complex (**1c**).

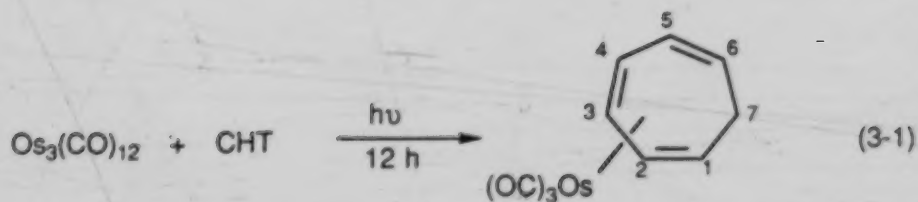
As the related Fe and Ru complexes (**1a**, **1b**) are known to be deprotonated by strong bases⁴⁻⁶, the isolation of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ (**1c**)

provides a route to the anionic complex, $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ (**2c**). Some chemistry of the group of compounds $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$ [$\text{M} = \text{Fe}$ (**2a**), $\text{M} = \text{Ru}$, (**2b**), $\text{M} = \text{Os}$, (**2c**)] has already been explored. In the case of Fe, these findings have provided some useful methodology for the synthesis of natural products containing seven-membered rings⁵. Additionally, these complexes react readily with inorganic electrophiles to produce metal-metal bonded complexes⁶ or to add substituents to the seven membered ring⁷. Reactions with the transition metal electrophiles $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M} = \text{Rh}$, Ir), in an attempt to produce cycloheptatrienyl bridged OsRh and OsIr complexes, will be described in a later chapter. In this chapter, the preparation, and some elementary reactions of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ are described.

3.2. Results.

3.2.1. Preparation of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$.

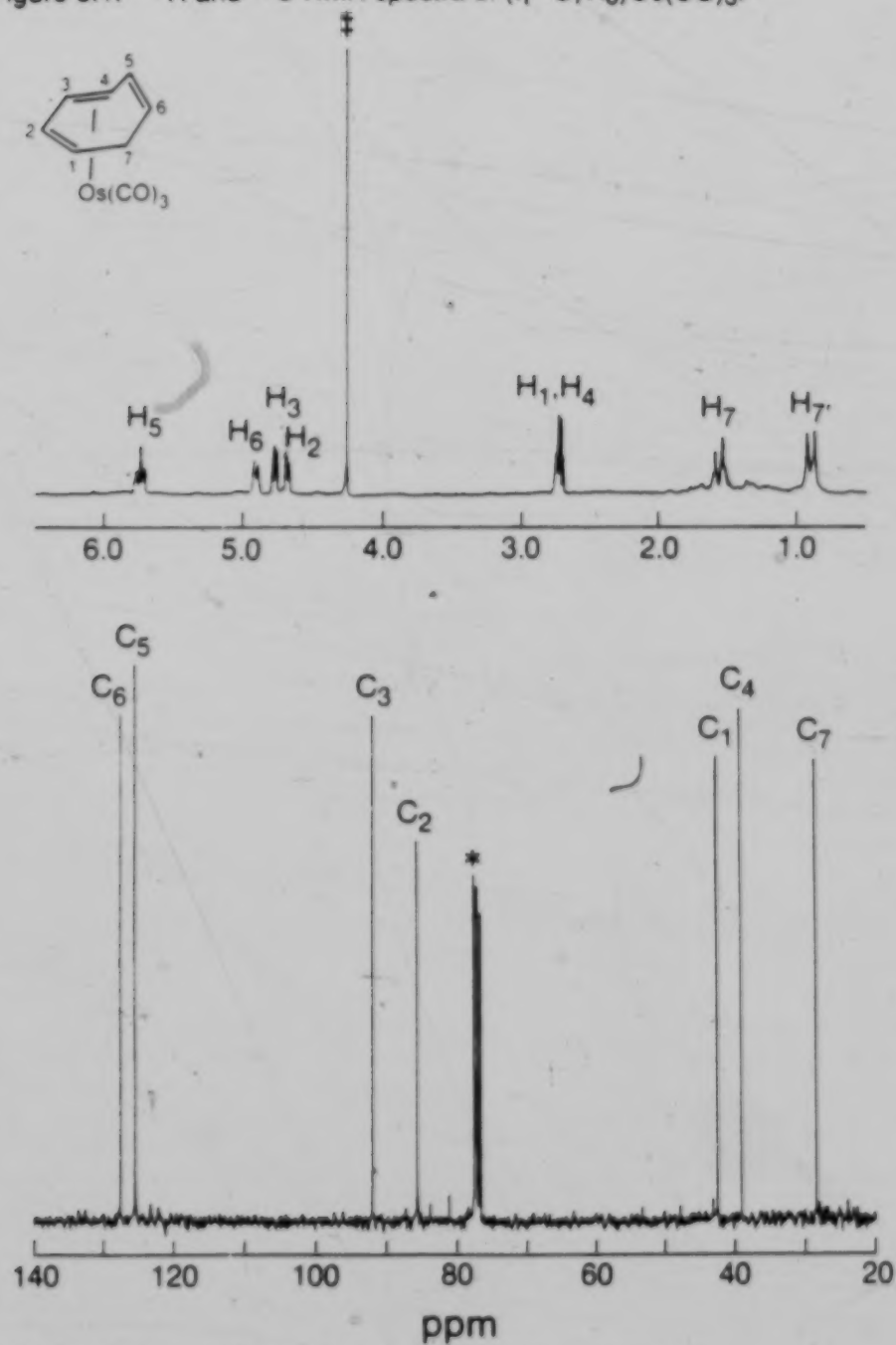
At the start of this work, the synthesis of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ (**1c**) had been accomplished in 80% yield starting from $\text{Os}(\text{CO})_5$ and cycloheptatriene (CHT)⁸. This procedure however, requires the preparation of $\text{Os}(\text{CO})_5$ from $\text{Os}_3(\text{CO})_{12}$ and hence a more convenient synthesis of **1c** directly from $\text{Os}_3(\text{CO})_{12}$ was sought. It was found that an overnight photolysis of $\text{Os}_3(\text{CO})_{12}$ and CHT in benzene gave a yellow solution. The IR spectrum of this solution indicated that the required $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ was the major product.



The reaction was cleanest when efficient cooling of the benzene solution was allowed in order to avoid reflux. This was accomplished by stirring the solution in a reaction vessel with a large surface area for the volume of solvent and placing the lamp inside a water-cooled quartz immersion well at least 10 cm from the reaction vessel. This method allows dissolution of $\text{Os}_3(\text{CO})_{12}$ and hinders competitive thermal reaction pathways. The drawback of this procedure is that it limits the quantity of solvent that can be used. This, combined with the low solubility of $\text{Os}_3(\text{CO})_{12}$ in benzene limits the amount of $\text{Os}_3(\text{CO})_{12}$ to about 0.3 g in 100 ml solvent. Under these conditions, most of the starting material has dissolved after about three hours photolysis, probably due to the unavoidable warming of the solution from the absorbed irradiation. After 12 hours the reaction is essentially complete. Solvent removal gives a yellow brown oil which can be purified by chromatography. When this is carried out, two bands become visible; the first band is pale yellow in colour, and this is followed directly by an orange band. The pale yellow band, which corresponds to the desired product, was eluted with pentane. The following band is thought to be a mixture of trinuclear compounds. Mixtures of polynuclear compounds have been observed in the thermal reaction between CHT and $\text{Ru}_3(\text{CO})_{12}$ ⁹. However, when one monitors the

eluted solvent by IR spectroscopy, it becomes apparent that in the colourless solvent prior to the first visible band there are small amounts of carbonyl containing compounds. Again, by analogy to the types of compounds obtained from the thermal reaction between CHT and $\text{Ru}_3(\text{CO})_{12}$, it is thought that these are due to a mixture of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ and $(\eta^4\text{-C}_7\text{H}_{10})\text{Os}(\text{CO})_3$. No attempt was made to isolate and identify the by-products.

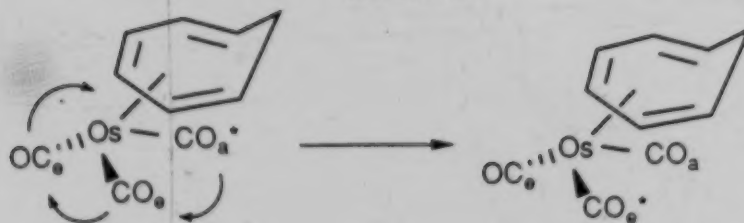
Removal of the pentane solvent from the desired fraction gave a pale yellow-green oil which was purified further by vacuum distillation at room temperature to a dry-ice cooled probe. This procedure eliminates the baseline impurities which are often visible in the IR spectrum of the compound after chromatography, and gives the pure product in about 60% yield. The IR spectrum of (1c) as expected gives three bands in hexane at 2066, 1994, 1984 cm^{-1} . The ^1H and ^{13}C NMR spectra in the cycloheptatrienyl region are shown in Figure 111. The spectra display signals due to a rigid seven-membered ring in similar fashion to those reported for the related Fe and Ru complexes^{9,10}. There is also a weak, broad signal in the ^{13}C NMR spectrum at 176.3 ppm due to the CO groups on Os. This indicates that the $\text{Os}(\text{CO})_3$ group is rotating whilst the seven-membered ring is static (see Scheme 3.1). This feature of the compound is expected from the known fluxional behaviour of related (diene) $\text{Fe}(\text{CO})_3$ compounds¹².

Figure 3.1. ^1H and ^{13}C NMR spectra of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$.^a

^a ^1H NMR recorded in C_6D_6 ; ^{13}C NMR recorded in CDCl_3

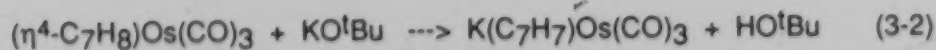
‡ = residual CH_2Cl_2 ; * = solvent.

Scheme 3.1



3.2.2. Reactivity of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ with bases. Preparation of $\text{K}(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3$.

Prior to this work the preparation of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ had been accomplished from $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ (**1c**) and KO^tBu . In order to further study the chemistry of **1c** and to possibly find more convenient deprotonating agents, **1c** has been reacted with several alternative bases. It was found that **1c** was not as acidic as the analogous Fe and Ru complexes. For instance, in contrast to Fe and Ru, no reaction occurred when a toluene solution of **1c** was stirred with $\text{Na}[(\text{Me}_3\text{Si})_2\text{N}]$ at room temperature over 24 hours. Additionally, no carbonyl containing products were observed in the room temperature reaction of **1c** with KH in THF solution¹³. The attempted deprotonation of **1c** using BuLi is discussed later in this chapter. Consequently, as in the case of Ru, the most convenient base was found to be KO^tBu . Upon addition of one equivalent of KO^tBu to $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ at room temperature, the yellow-green THF solution rapidly turns to a bright orange colour.



The IR spectrum of the bright orange solution [1961 (s), 1884 (s), 1863 (sh)] shows the expected shift to lower energy from the starting material. As shown in Figure 3.2, the room temperature ^1H NMR spectrum shows a single peak for the C_7H_7 ligand. This is expected for rapid rotation of the seven membered ring. This process, which is stopped at -100°C , will be commented upon more fully in Chapter 5. In the room temperature ^{13}C NMR spectrum, there is a single peak for the C_7H_7 ligand, and one sharp resonance for all three CO groups on the Os centre.

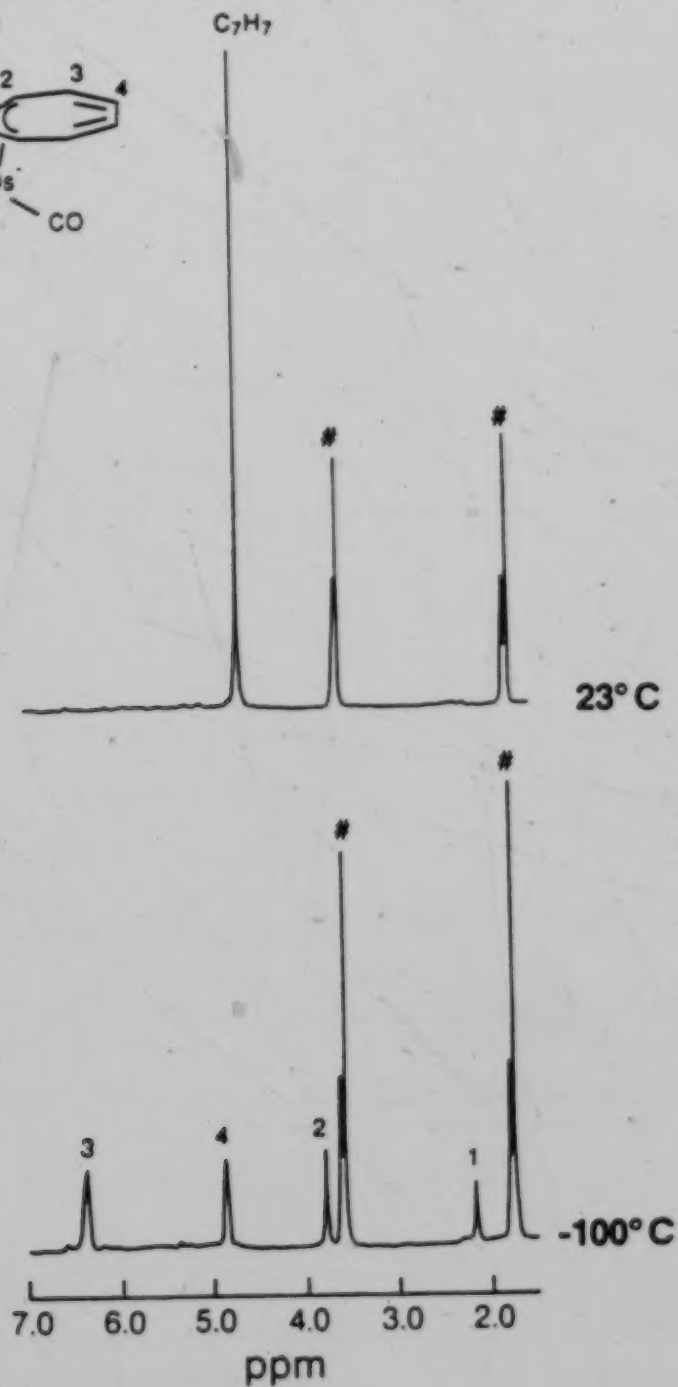
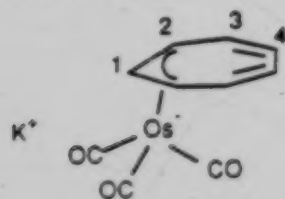
One surprising observation about this reaction was that it was found to be temperature dependent: Thus, when a dark orange solution of $\text{K}(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3$ (**2c**), prepared from reaction of **1c** with KO^tBu at room temperature, is allowed to stir at -78°C the solution will regain the original pale yellow-green colour and IR spectroscopy indicates substantial reformation of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ (equation 3-3). This led to



complications in some reactions of **2c**, as a minor pathway was often reprotonation to give back **1c**. For this reason, in certain instances it was deemed desirable to isolate the anion in the solid state in the absence of HO^tBu , and hence the preparation and isolation of $[\text{Ph}_4\text{As}][(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ was carried out.

Figure 3.2. Room Temperature and -100 °C ^1H NMR Spectra of 2c.

= residual THF



3.2.3. Preparation of $[\text{Ph}_4\text{As}][(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]$.

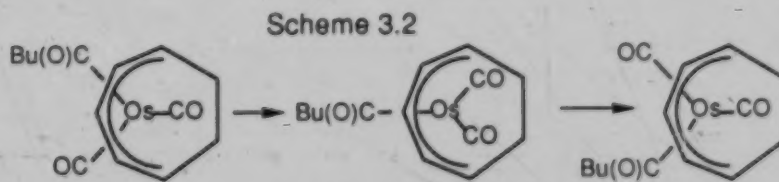
Crystals of the AsPh_4^+ salt of the Os anion, were prepared by reaction of a freshly made THF solution of $\text{K}(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3$ with AsPh_4Cl . Upon addition of the anionic solution to a slurry of AsPh_4Cl in THF at room temperature, most of the suspension dissolves to give a dark red solution of $[\text{Ph}_4\text{As}][(\text{C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ and a precipitate of KCl. The IR spectrum of the supernatant solution [1963 (s), 1883 (s), 1864 (s)] indicates complete cation exchange by the much sharper bands for the carbonyl stretching vibrations¹⁴. Separation of the supernatant solution followed by filtration and rapid crystallization from THF/toluene gives dark red crystals of $[\text{Ph}_4\text{As}][(\text{C}_7\text{H}_7)\text{Os}(\text{CO})_3]\cdot\text{THF}$. The maximum yield obtained as crystals is about 40 % as the compound has a tendency to form an oil in the presence of any slight impurities such as $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$.

3.2.4. Reaction of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ with BuLi.

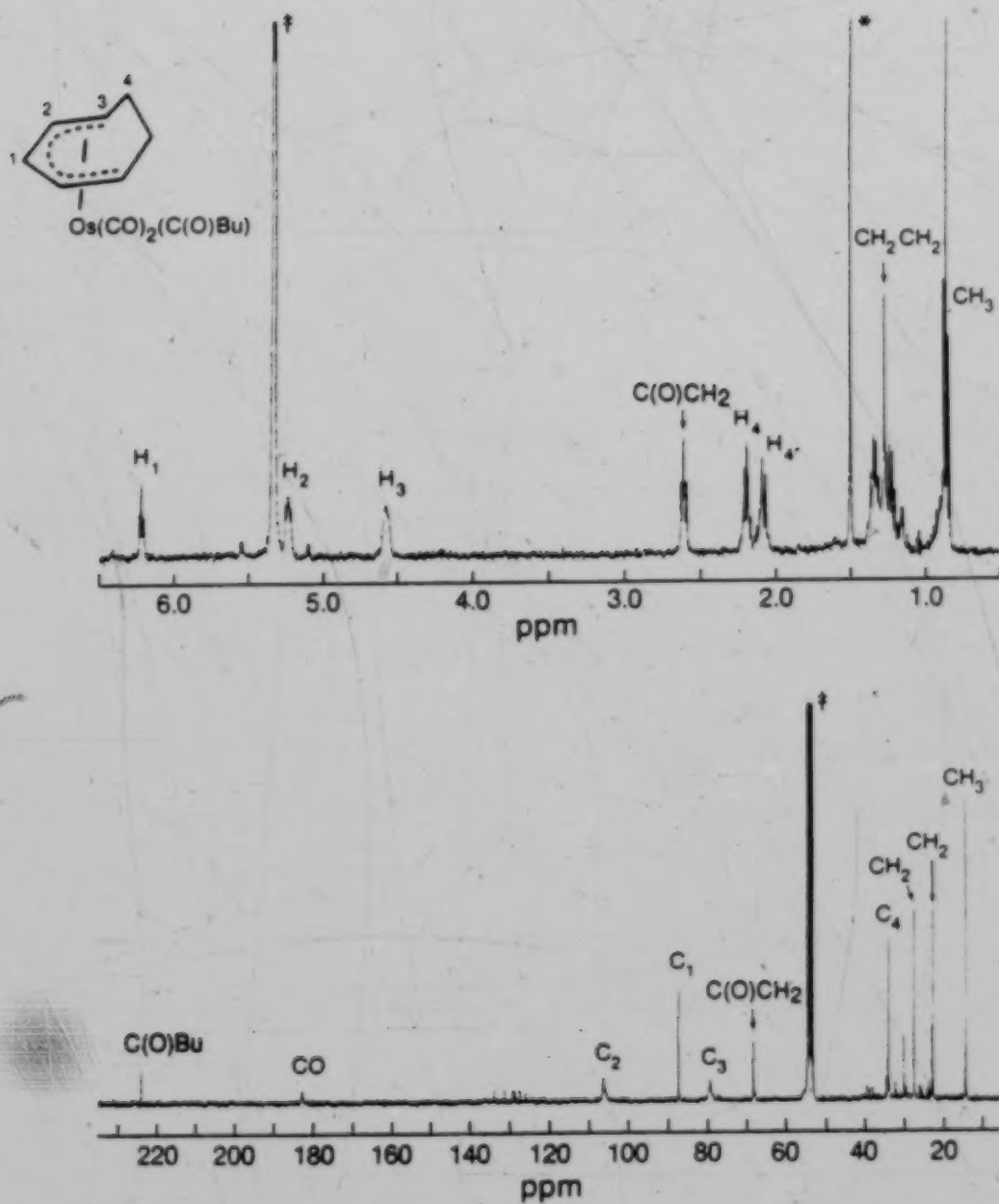
Addition of one equivalent of BuLi to a THF solution of **1c** gave a colour change from pale yellow-green to yellow-orange as expected for formation of an anionic complex. Surprisingly the IR showed only two sharp bands at 1955 and 1883 cm^{-1} which contrasts with $\text{K}(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3$ [1961 (s), 1884 (s), 1863(sh)]. Addition of this anion to $[\text{Ir}(\text{COD})\text{Cl}]_2$ failed to give a clean reaction. Following this experiment, the ^1H NMR spectrum of the anionic complex was run. Instead of the expected single peak for $\text{Li}(\text{C}_7\text{H}_7)\text{Os}(\text{CO})_3$, a very complicated spectrum was obtained indicating that a different product had been formed. This was verified when hydrolysis of the anion followed by work-up gave a light green oil (**3c**)

which was determined not to be $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$. The ^1H and ^{13}C NMR spectra of **3c** are shown in Figure 3.3. It can be seen that there are too many peaks to be assigned to a single C_7H_7 ring. The structure as depicted in the figure was deduced from homonuclear decoupling experiments. Assignments of the ^{13}C signals were according to literature reports of cycloheptadienyl¹⁵ and acyl¹⁶ compounds.

It can be seen from the figure that two of the ring signals (H_2 and H_3) have a slightly broad nature. This is also reflected in the ^{13}C NMR spectrum of the respective signals. The broad nature of two of the signals can be explained by interconversion of the two enantiomeric forms of the asymmetric isomer. This is accomplished by rotation of the $\text{Os}(\text{CO})_2[\text{C}(\text{O})\text{Bu}]$ group with respect to the C_7H_9 ligand (Scheme 3.2)¹⁵. Consistent with this postulate, the CO resonance is also broad due to the exchange of two distinct resonances. In the symmetric isomer, only one sharp resonance would be expected.

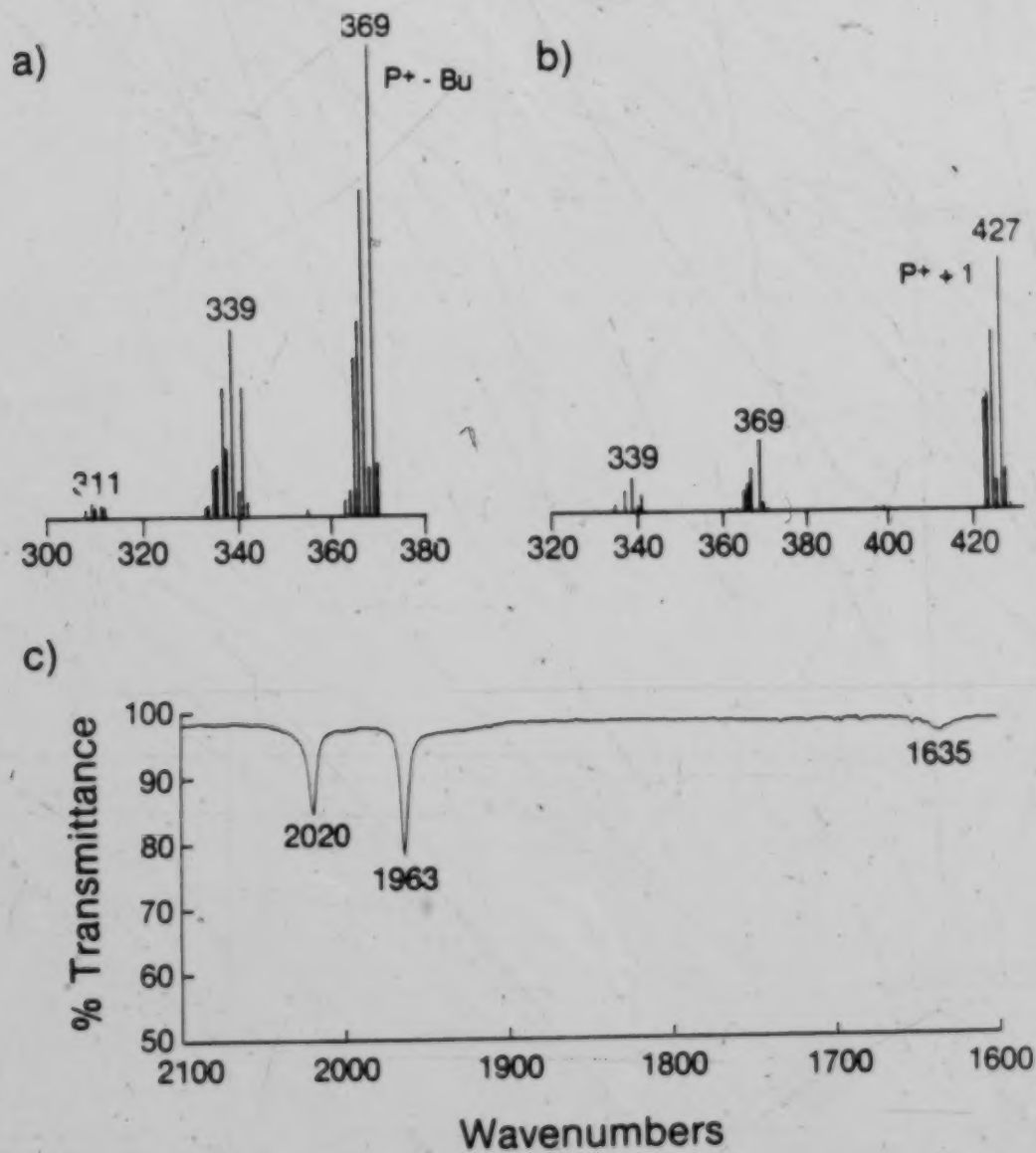


The IR spectrum for **3c** (Figure 3.4) shows two strong bands in the terminal CO stretching region at 2020 and 1963 cm^{-1} (hexane).

Figure 3-3 ^1H and ^{13}C NMR Spectra of $(\eta^5\text{-C}_7\text{H}_9)\text{Os}(\text{CO})_2[\text{C}(\text{O})\text{Bu}]^a$ 

a Spectra recorded in CD_2Cl_2 ; $\ddagger$ = solvent * = unidentified impurity.

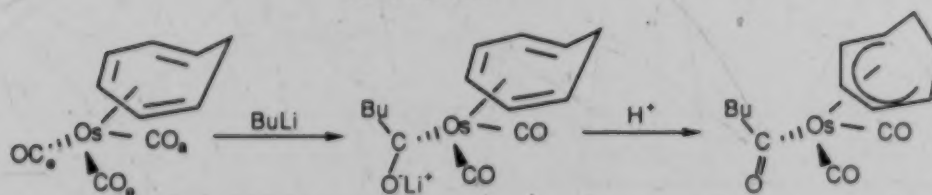
Figure 3.4. Mass Spectra (a,b) and IR spectrum in the carbonyl region (c) of $(\eta^5\text{-C}_7\text{H}_9)\text{Os}(\text{CO})_2[\text{C}(\text{O})\text{Bu}]$.



a) electron impact (16 eV, 100 °C), b) chemical ionisation (NH_3)

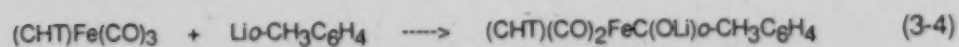
A weak band outside the terminal CO stretching region due to the acyl CO group can also be observed at 1635 cm^{-1} . The observation of only two strong bands in hexane solution at very similar frequencies has also been seen for several closely related acyl compounds $\text{Cp}(\text{OC})_2\text{Fe}(\text{C}(\text{O})\text{R})$ ($\text{R} = \text{aryl}$)¹⁷. The electron impact and chemical ionization mass spectra of **3c** are also shown in Figure 3.4. The electron impact mass spectra has large peaks due to $(\text{P}^+ - \text{Bu})$ (most intense peak = 369). In addition the cluster of peaks centred at 339 is due to $(\text{P}^+ - \text{Bu} - \text{CO})$ (most intense peak = 341) and $(\text{P}^+ - \text{Bu} - \text{CO} - \text{H}_2)$ (most intense peak = 339). The ready loss of alkyl groups on acyl substituents has previously been observed¹⁶. In addition, strong peaks due to $(\text{M}^+ - \text{CO} - \text{H}_2)$ are typical of exo substituted cyclohexadiene compounds¹⁸. Using chemical ionization (NH_3) as the ionization method, the cluster of peaks due to the parent ion at 427 ($\text{P}^+ + 1$)¹⁹ is observed. The MS data were simulated using a locally available program. The mechanism of formation of this compound, which is discussed further in the next section, is most likely nucleophilic attack at the carbonyl ligand, followed by protonation at the C_7H_8 ligand as shown below.

Scheme 3.3



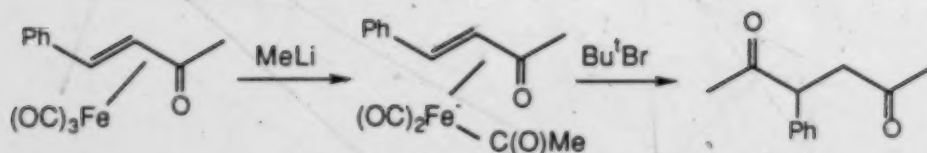
3.3. Discussion

It may appear surprising that the reaction of **1c** with BuLi is different from that observed for the analogous Fe and Ru compounds. However, it has previously been observed in (dienyl)M(CO)₃ cations that nucleophilic attack at CO is more prone for M = Os than for M = Fe²⁰. One possible reason for this, is that in the case of Os there is more negative charge delocalised onto the CHT ligand than onto the carbonyl ligands, making nucleophilic attack at CO more amenable. Nucleophilic attack of BuLi on carbonyl groups of both Os and Ru cluster compounds leading to stable acyl anions has been previously observed²¹. In addition, nucleophilic attack by aryl lithium compounds has been seen on (η⁴-C₇H₈)Fe(CO)₃²²:



A series of acylate iron complexes has been prepared in this fashion. This, of course, contrasts to the deprotonation which occurs when BuLi is used in place of Li-o-CH₃C₆H₄²³. In addition, and also very recently, butyl lithium has been observed to react in similar fashion with related tricarbonyl iron complexes of α,β-unsaturated ketones²⁴. Rearrangement of the resultant acylate compounds upon reaction with Bu^tBr ultimately gives products useful in organic synthesis.

Scheme 3.4.



The second step in the formation of **3c** is the hydrolysis of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_2\text{C}(\text{OLi})\text{Bu}$. In this reaction, protonation occurs at the seven-membered ring instead of the acylate group. This is consistent with the known reactivity of $(\text{cyclooctatetraene})\text{Fe}(\text{CO})_2\text{C}(\text{OLi})(\text{aryl})$ ²⁵ where, upon reaction with $[\text{Et}_3\text{O}][\text{BF}_4]$ in H_2O at 0°C (or in CH_2Cl_2 at -30°C), protonation at the ring is the favoured pathway.

The complexes **2c**, **1c**, and **3c**; $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3$, $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$, and $(\eta^5\text{-C}_7\text{H}_9)\text{Os}(\text{CO})_2\text{C}(\text{O})\text{Bu}$ provide an interesting series of complexes with increasing coordination to an unsaturated seven-membered ring. The variable temperature ^1H and ^{13}C NMR spectra of these complexes thus affords information about the changing interaction between the metal centre and the seven-membered ring within this series. As already mentioned, and as expected²⁶, very rapid fluxional behaviour of the C_7H_7 ring and $\text{Os}(\text{CO})_3$ group is observed for **2c**. This will be discussed more fully in Chapter 5. Complexes **1c** and **3c**, again as expected, show decreased fluxional behaviour. No ring movement is observed for **1c**. A net 1,3 shift motion is possible²⁷ however, it is not expected to occur at room temperature²⁸. No such process is available for

3c due to the lack of uncoordinated sites of unsaturation in the seven-membered ring. Interestingly, both **1c** and **3c** display a broad signal in their ^{13}C NMR spectra for the CO resonances at room temperature indicating both are undergoing a rotation of the $\text{Os}(\text{CO})_2\text{L}$ group with respect to the seven membered ring at close to the same rate. In the related complex, $(\eta^4\text{-C}_7\text{H}_8)\text{M}(\text{CO})_3$ ($\text{M} = \text{Ru}$) a very similar observation was made²⁹. However, for the analogous iron complex ($\text{M} = \text{Fe}$), a fairly sharp singlet for the three carbonyl groups was observed which broadens only when the sample is cooled below 0°C ¹². This indicates that the process may be slightly more facile for Fe, which, of course, is in accord with the well-known increase in metal-ligand bond strengths³⁰ as a transition metal triad is descended.

3.4. Experimental.

3.4.1. General Techniques and Reagents, Chapter 3.

$\text{Os}_3(\text{CO})_{12}$ was prepared according to the literature³¹.

Cycloheptatriene and tetraphenylarsonium chloride hydrate were purchased from Aldrich Chemical Company. Cycloheptatriene was distilled prior to use, and tetraphenylarsonium chloride hydrate was dehydrated by evacuation (10^{-3} mm Hg) at 110°C for 24 hours, or until no further weight loss was observed. Butyl lithium was bought from Aldrich Chemical Company as a 1.6 M solution in hexanes. Elemental analyses on oils **1c** and **3c** were not attempted due to difficulties in separation from solvents.

3.4.2. Typical Synthesis of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$, **1c**.

$\text{Os}_3(\text{CO})_{12}$ (0.28 g), cycloheptatriene (6 ml) and C_6H_6 (90 ml) were placed in a pyrex 3 x 18 cm Schlenk tube which was purged with N_2 for 10 minutes and then fitted with a water cooled condenser. The pale green solution was placed 11 cm from a 450 W high pressure Hanovia mercury lamp and the solution was then irradiated for 12 hours with shielding of the lamp and vessel by aluminium foil on only one side. The solvent was removed from the resultant yellow solution to leave a yellow brown residue which was chromatographed on a silica gel column (3 cm x 5 cm, Merck, Kieselgel 60, 230 - 400 mesh) with pentane. A pale yellow-green band due to $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ was easily visible. This band was followed by a slow moving orange band. The eluent was collected from

the beginning of the pale yellow-green band until the beginning of the orange band. The solvent was then removed to obtain a pale yellow-green oil (0.18 g, 62%). Further purification could be accomplished by distillation under vacuum at room temperature to a dry-ice cooled probe. The solid could then be washed from the probe with pentane into a separate flask. Removal of the solvent afforded $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ as a pale yellow-green oil (0.16 g, ca. 55%).

IR ν_{CO} (hexane) 2066, 1994, 1982 cm^{-1} .

^1H NMR: (22 °C, CD_2Cl_2); δ 5.74 (1H,m, H_5) 4.91 (1H,m, H_6), 4.77 (1H,m, H_3), 4.68 (1H,m, H_2), 2.72 (2H,m, H_1+H_4), 1.56 (m, H_7), 0.89 (m, H_7).

For numbering scheme see text.

3.4.3. Synthesis of $[\text{AsPh}_4][(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]$, 2c.

$\text{K}[(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ in THF (15 ml) was made directly from $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ (85 mg, 0.23 mmoles) and KO^tBu (26 mg, 0.23 mmoles)⁸. The dark red solution was transferred under nitrogen to a separate flask containing a slurry of AsPh_4Cl (97 mg, 0.23 mmoles) in THF (15 ml). The solution was filtered and then the solvent was removed to leave a dark orange residue which was redissolved in THF and crystallised rapidly at room temperature by addition of toluene to give dark red crystals of $[\text{AsPh}_4][(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]\cdot\text{THF}$ (70 mg, 41%). The inclusion of one molecule of THF was determined from integration of the ^1H NMR spectrum in CD_2Cl_2 .

Anal. Calcd for $\text{C}_{38}\text{H}_{35}\text{AsO}_4\text{Os}$: C, 55.55, H, 4.29. Found: C, 55.80; H, 4.38.

IR (THF) ν_{CO} : 1963(s), 1883(s), 1864(s) cm^{-1} .

^1H NMR (25 $^{\circ}\text{C}$, THF- d_8): δ 7.7 - 7.9 (20H, Ph) 4.66 (s, 7H, C_7H_7); (-115 $^{\circ}\text{C}$): 6.42 (m, 2H, H_3), 4.87 (dd, $J_{\text{H}_3-\text{H}_4}=8.3$, 3.7 Hz, 2H, H_4), 3.83 (dd, $J_{\text{H}_2-\text{H}_3}=7.5$ Hz; $J_{\text{H}_1-\text{H}_2}=7.5$ Hz, 2H, H_2), 2.19 (t, $J_{\text{H}_1-\text{H}_2}=4.5$ Hz, 1H, H_1).

^{13}C [^1H] NMR (25 $^{\circ}\text{C}$, THF- d_8): δ 191.9 (s, CO), 135.3 (s, Ph, p) 134.4 (s, Ph), 131.8 (s, Ph), 89.2 (s, C_7H_7); (-110 $^{\circ}\text{C}$): 142.0 (s, C_7H_7 , C_3) 111.9 (s, C_7H_7 , C_4), 37.9 (s, C_7H_7 , C_1+C_2).

3.4.4. Reaction of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ with Butyl Lithium and Subsequent Hydrolysis.

1c (130 mg, 0.36 mmoles) was dissolved in a 100 ml reaction vessel in THF (15 ml) under nitrogen. To this pale green solution was added 0.25 ml of 1.6 M butyl lithium solution in hexane (0.40 mmoles) from a new bottle. This gave a yellow-orange solution to which was added three drops of water. The solution lightened and was then extracted in hexane and dried over Na_2SO_4 . The solvent was removed to give a yellow-brown residue which was chromatographed on silica gel (CH_2Cl_2 /acetone; 25:1) and then vacuum distilled to give a pale green oil (60 mg, 40%).

IR (hexane) ν_{CO} : 2020 (s), 1963 (s), 1635 (w) cm^{-1} .

^1H NMR: (22 $^{\circ}\text{C}$, CD_2Cl_2) δ 6.22 (1H, t, $J=6$ Hz, H_1), 5.24 (2H, br, m, $\text{H}_{2/2'}$), 4.58 (2H, br, m, $\text{H}_{3/3'}$), 2.62 (2H, m, $\text{C}(\text{O})\text{CH}_2$), 2.20 (2H, m, H_4), 2.08 (2H, m, $\text{H}_{4'}$), 1.34 (2H, m, CH_2), 1.25 (2H, m, CH_2), 0.88 (3H, m, CH_3).

^{13}C NMR: (22 $^{\circ}\text{C}$, CD_2Cl_2) δ 224 ($\text{C}(\text{O})\text{Bu}$), 183 (br, CO), 106.2 (br, $\text{C}_{2/2'}$), 87.3 (C_1) 79.2 (br, $\text{C}_{3/3'}$), 68.1 ($\text{C}(\text{O})\text{CH}_2$), 34.0 ($\text{C}_{4/4'}$), 27.4, 22.6 (CH_2), 14.2 (CH_3).

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Chapter 4.

Reaction of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ with $[\text{M}(\text{COD})\text{Cl}]_2$ ($\text{M} = \text{Rh}, \text{Ir}$).

Formation, Characterization and Derivatization of Isomeric *cis*- and *trans*-($\mu\text{-C}_7\text{H}_7$) $\text{Os}(\text{CO})_3\text{M}(\text{COD})$ Complexes.

4.1 Introduction.

Of the many useful synthetic reactions available to anionic carbonyl complexes of the transition metals, a particularly important and currently topical application is the ability to produce heterobimetallic complexes upon reaction with suitable electrophilic transition metal substrates¹. As already mentioned in this thesis, we have for some time been involved in the chemistry of the ambident organometallic nucleophiles $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$ ($\text{M} = \text{Fe}, \mathbf{1a}, \text{Ru}, \mathbf{1b}$). Thus reaction of $\mathbf{1a}$ with group 14 electrophiles R_3SiCl and R_3GeBr gives ring substituted complexes², whereas reaction of $\mathbf{1a}$ and $\mathbf{1b}$ with $[\text{M}'(\text{COD})\text{Cl}]_2$ ($\text{M}' = \text{Rh}, \text{Ir}$)³ leads to the formation of cycloheptatrienyl bridged heterobimetallic complexes; *cis*-($\mu\text{-C}_7\text{H}_7$) $\text{M}(\text{CO})_3\text{M}'(\text{COD})$ ($\text{M-M}'$) ($\text{M}' = \text{Rh}, \text{Ir}$; COD = 1,5-cyclooctadiene), in which both metals are situated on the same side of the seven-membered ring.

As described in Chapter 2, the synthesis of the anionic osmium complex $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ ($\mathbf{1c}$) has been accomplished and its structure is compared to that of the analogous Fe and Ru derivatives in

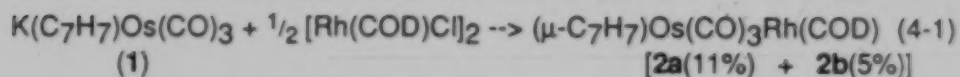
Chapter 5⁴. In brief, it was found that in the solid state all three compounds contain an η^3 -bound cycloheptatrienyl moiety and it is believed that the $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$ formulation is maintained in solution as well. Accordingly, **1c** reacts with Ph_3SnCl to give the anticipated product, $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{SnPh}_3$ ⁵ containing an Os-Sn bond. However, unexpectedly and in contrast to Fe and Ru, the reaction of the osmium anion with $[\text{M}'(\text{COD})\text{Cl}]_2$ ($\text{M}' = \text{Rh}, \text{Ir}$) gives heterobimetallic complexes where the two metal fragments occupy opposite faces of the bridging cycloheptatrienyl moiety, *trans*-($\mu\text{-C}_7\text{H}_7$) $\text{Os}(\text{CO})_3\text{M}'(\text{COD})$ ($\text{M}' = \text{Rh}$, **2a**, Ir , **3a**) as the initial product. Subsequent isomerization yields the thermodynamically more stable, and ubiquitous product of previous reactions, *cis*-($\mu\text{-C}_7\text{H}_7$) $\text{Os}(\text{CO})_3\text{M}'(\text{COD})$ ($\text{M}' = \text{Rh}$, **2b**, Ir , **3b**). In this chapter, the synthesis, characterization, and structure of complexes **2** and **3**, are described, and a detailed triad comparison of the fluxional solution behaviour of the thermodynamically more stable *cis*-($\mu\text{-C}_7\text{H}_7$) $\text{M}(\text{CO})_3\text{M}'(\text{COD})$ compounds ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$; $\text{M}' = \text{Rh}, \text{Ir}$) is also given.

4.2 Results

4.2.1 Reaction of $\text{K}(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ with $[\text{Rh}(\text{COD})\text{Cl}]_2$.

The reaction of $\text{K}[(\text{C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ (**1c**) with $[\text{Rh}(\text{COD})\text{Cl}]_2$ at -78°C in THF solution followed by solvent removal at room temperature leads to the isolation of two new products, in addition to a small amount of the reformed starting material, $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$. The mass spectra and

elemental analyses of these new compounds, separated by fractional crystallization, identified them as two isomers of the expected product: $(\mu\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{Rh}(\text{COD})$ (**2**).

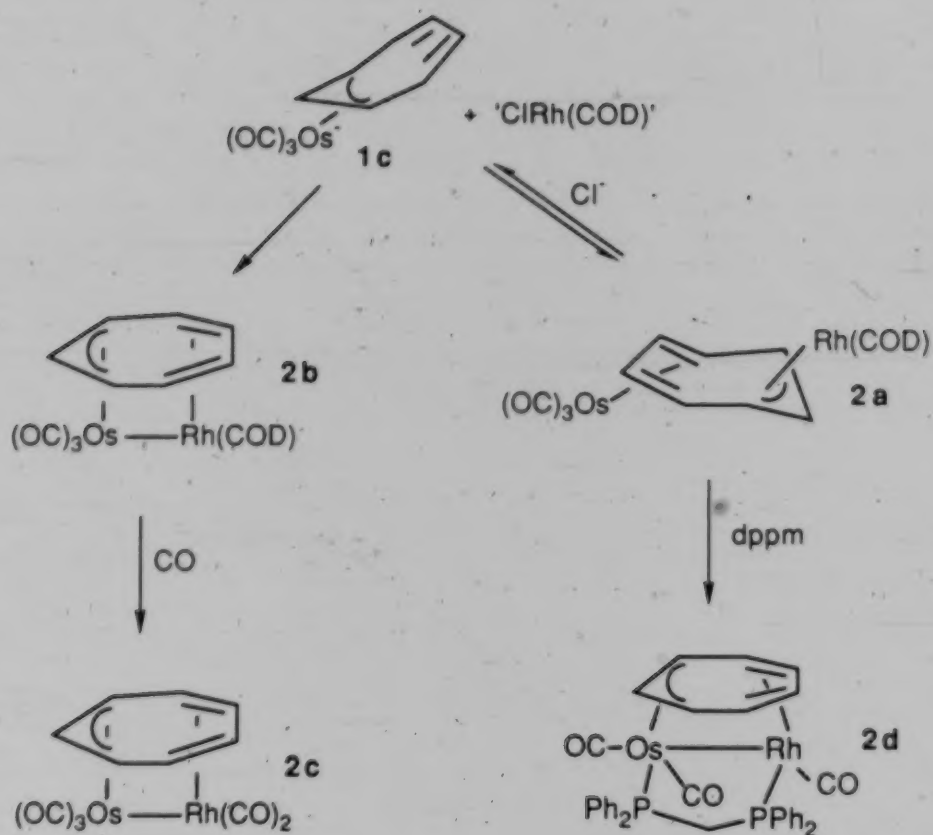


The IR spectrum of one of these compounds (**2b**) (2030, 1962, 1957 cm^{-1}) is very close to the expected spectrum for *cis*- $(\mu\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{Rh}(\text{COD})$. Compound **2b** is a bright orange, air stable solid which can be purified further by chromatography. In contrast the larger yield product (11%, **2a**) is more sensitive to air or trace impurities and does not survive chromatography. This product was crystallised from CH_2Cl_2 /hexane over 12 hours at -40°C and was obtained as a tan-yellow microcrystalline solid which can be stored for several days in the solid state under inert atmosphere without noticeable decomposition. Darkening of the compound does occur at room temperature after more prolonged periods. The IR spectrum of this compound in the carbonyl region (2060, 1991, 1979 cm^{-1}) is very close to that observed for $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$, (2066, 1994, 1982 cm^{-1}). On the basis of these observations this compound (**2a**) was assigned to be *trans*-($\mu\text{-C}_7\text{H}_7$) $\text{Os}(\text{CO})_3\text{Rh}(\text{COD})$ and **2b** was assigned to be its *cis* isomer.

When the reaction was repeated in diethyl ether and the reaction mixture was not allowed to warm above -10°C the yield of **2a** was

doubled. In this reaction, only a trace amount of **2b** was formed implying that the *cis* compound may have been formed via isomerization of **2a** during attempted work up. When the reaction was carried out using the Ph_4As^+ salt of **1** instead of K^+ the reaction followed a different path. Again the initial product appeared to be **2a**, based on IR spectroscopy. However, upon warming to room temperature, work up of the orange residue did not give any **2a**, but yielded 25% of *cis* compound **2b** in addition to a small amount of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$. This indicated that in this reaction the isomerization of **2b** to **2a** had been much cleaner presumably due to the presence of AsPh_4Cl in solution. To account for this, and the significant increase in yield we suggest that the increased concentration of chloride ion in solution can act as a catalyst in this process as shown in Scheme 4.1. This hypothesis was strengthened when the reaction of **2a** with 0.5 equivalents of PPNCl was carried out. The THF solution darkened from yellow to orange-brown and complete consumption of starting material had occurred after stirring for 15 minutes at room temperature. Although the reaction was not clean, the major product (25%) was **2b**, with a small amount of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ also visible in the IR spectrum of the hexane extract. There were apparently no other carbonyl containing products formed. The variable temperature ^1H and ^{13}C NMR spectra of compounds **2** (*vide infra*) were consistent with these assignments however in view of the unexpected results it was deemed necessary to confirm the assignments by X-ray structural characterization.

Scheme 4.1 Preparation of OsRh Heterobimetallic Compounds.



4.2.2. Solid State Structure of 2a.

X-ray quality crystals of **2a** were obtained by crystallization from CH_2Cl_2 /hexane (1:1) at -40°C for 2 days under inert atmosphere. This produced a small amount of thin yellow plates. The molecular structure of **2a** was determined from one of the thickest crystals by Dr. B. D. Santarsiero of the Structure Determination Laboratory of this department. The structure is shown in Figures 4.1 and 4.2. Selected interatomic bond lengths and angles are given in Tables 4.1 and 4.2. As can be seen from Figure 4.1, the central seven-membered ring is separated into an allylic portion bonded to Rh, and a diene unit bonded to Os. The two parts of the C_7H_7 ring are separated by relatively long C-C bonds. The orientation of the ring can be referred to as being in a chair conformation. This conformation was also observed in the *trans*-(μ - η^3, η^4 - C_7H_7) complex, $\text{Cp}(\text{OC})_2\text{Mo}(\mu\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3$ ⁶. The main features of the seven-membered ring are very similar in both cases. Thus the allylic C-C bond lengths are typical at ca. 1.40 Å and the terminal allylic carbons are bonded to the outer diene carbons by long bonds of ca. 1.50 Å. Within the diene section of the seven membered ring the central bond is relatively short at 1.391 (18) Å. The two remaining outer diene C-C bonds are intermediate at ca. 1.45 Å. The $\text{Os}(\text{CO})_3$ group is bonded to the diene fragment in a close to symmetric fashion with distances to the outer diene carbons of 2.252 (10) (C3) and 2.232 (10) (C6) Å. The Os to inner carbon bond distances are shorter and approximately identical at ca. 2.18 Å. The Os centre thus can be thought of as having an approximate square-

Figure 4.1 Molecular Structure of 2a (Front View).

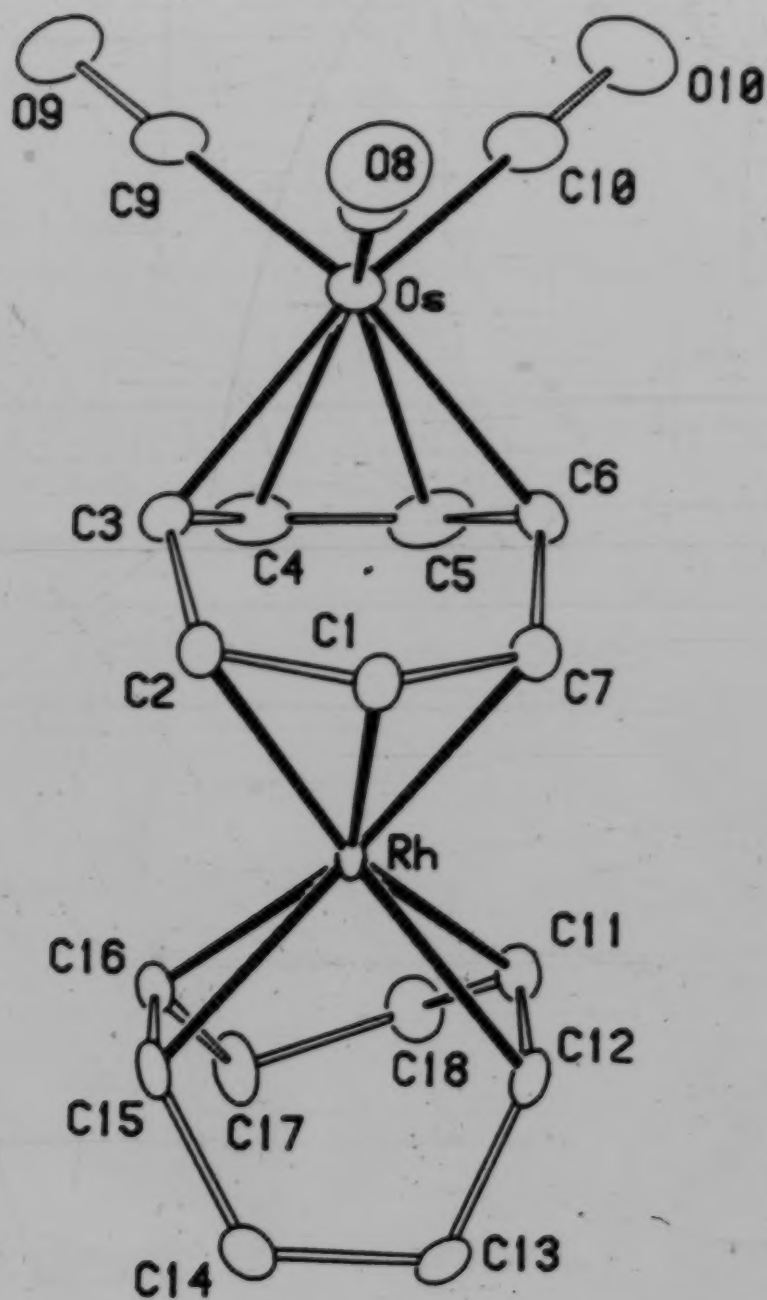


Figure 4.2.

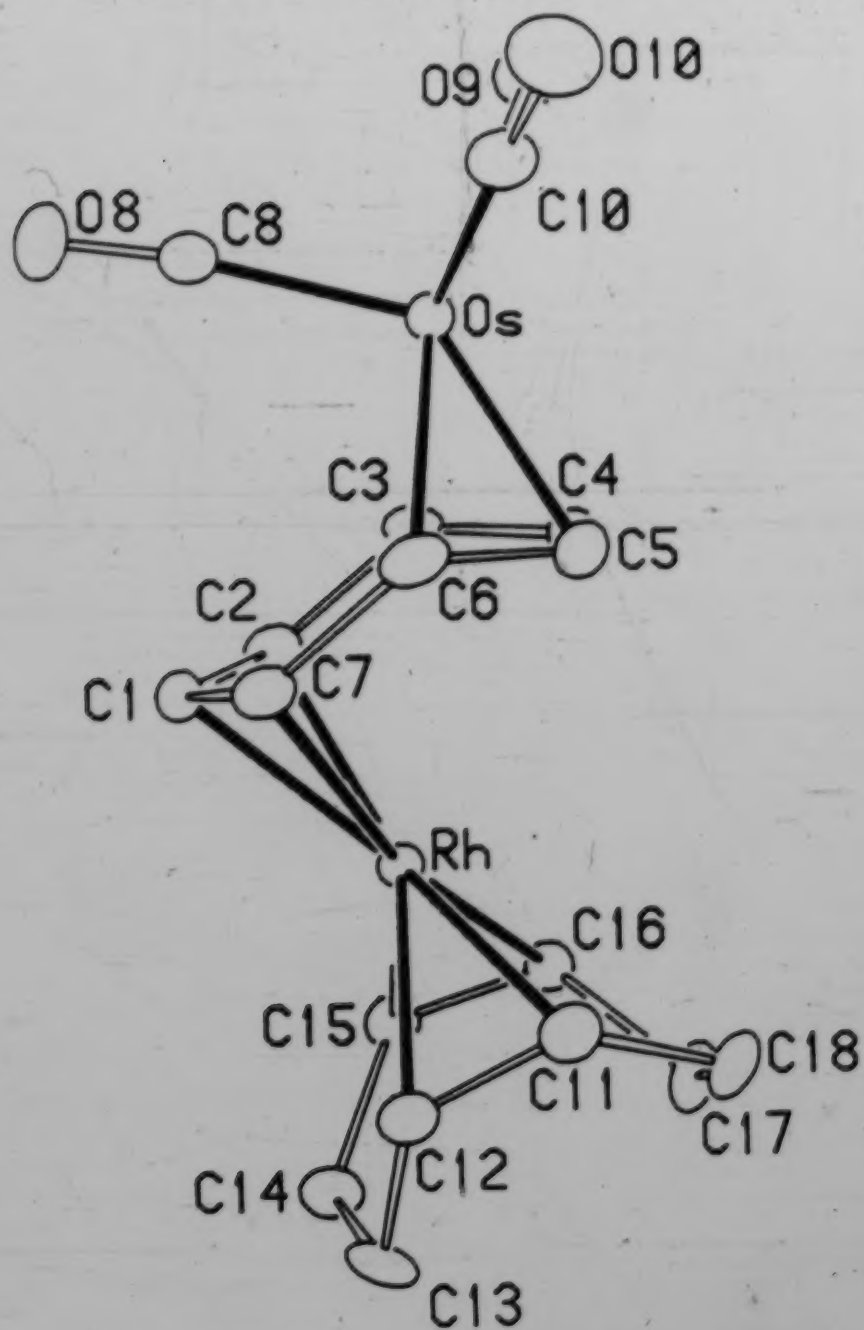
Molecular Structure of 2a showing chair conformation of C₇H₇ ring.

Table 4.1 Selected Interatomic Distances in 2a.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Os	C3	2.252 (10)	C1	C2	1.397 (13)
Os	C4	2.183 (10)	C2	C3	1.501 (13)
Os	C5	2.178 (10)	C3	C4	1.458 (15)
Os	C6	2.232 (10)	C4	C5	1.391 (18)
Os	C8	1.891 (10)	C5	C6	1.442 (16)
Os	C9	1.901 (12)	C6	C7	1.505 (14)
Os	C10	1.889 (13)	C7	C1	1.406 (13)
Rh	C1	2.151 (8)	C8	O8	1.132 (12)
Rh	C2	2.189 (8)	C9	O9	1.140 (13)
Rh	C7	2.209 (9)	C10	O10	1.158 (14)
Rh	C11	2.148 (9)	C11	C12	1.378 (13)
Rh	C12	2.137 (9)	C12	C13	1.484 (13)
Rh	C15	2.138 (9)	C13	C14	1.522 (14)
Rh	C16	2.159 (9)	C14	C15	1.501 (13)
			C15	C16	1.370 (12)
			C16	C17	1.531 (12)
			C17	C18	1.543 (14)
			C18	C11	1.507 (14)

*In Angstroms. Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 4.2 Selected Interatomic Angles in 2a.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Rh	C2	37.5 (3)	C1	C2	C3	125.4 (9)
C1	Rh	C7	37.6 (3)	C2	C3	C4	126.2 (9)
C1	Rh	C11	137.5 (4)	C3	C4	C5	119.7 (9)
C1	Rh	C12	119.2 (4)	C4	C5	C6	118.8 (10)
C1	Rh	C15	116.0 (3)	C5	C6	C7	126.3 (9)
C1	Rh	C16	140.3 (3)	C6	C7	C1	124.4 (9)
C2	Rh	C7	66.5 (4)	C7	C1	C2	118.8 (8)
C2	Rh	C11	162.8 (4)	C11	C12	C13	124.5 (9)
C2	Rh	C12	153.6 (4)	C12	C13	C14	112.9 (8)
C2	Rh	C15	97.9 (4)	C13	C14	C15	114.9 (8)
C2	Rh	C16	106.0 (4)	C14	C15	C16	124.9 (9)
C7	Rh	C11	102.3 (4)	C15	C16	C17	122.8 (9)
C7	Rh	C12	101.1 (4)	C16	C17	C18	112.0 (8)
C7	Rh	C15	151.0 (4)	C17	C18	C11	113.4 (8)
C7	Rh	C16	166.8 (4)	C18	C11	C12	126.2 (9)
C11	Rh	C12	37.5 (4)				
C11	Rh	C15	97.5 (4)				
C11	Rh	C16	82.1 (4)				
C12	Rh	C15	82.2 (4)				
C12	Rh	C16	90.1 (4)				
C15	Rh	C16	37.2 (3)				

Table 4.2 continued. Selected Interatomic Angles in 2a.

Atom1	Atom2	Atom3	Angle
C3	Oa	C4	38.4 (4)
C3	Oa	C5	67.5 (5)
C3	Oa	C6	77.5 (3)
C3	Oa	C8	96.1 (4)
C3	Oa	C9	92.3 (4)
C3	Oa	C10	163.8 (4)
C4	Oa	C5	37.2 (5)
C4	Oa	C6	67.0 (4)
C4	Oa	C8	132.9 (4)
C4	Oa	C9	96.6 (5)
C4	Oa	C10	125.8 (5)
C5	Oa	C6	39.1 (4)
C5	Oa	C8	133.9 (4)
C5	Oa	C9	125.4 (5)
C5	Oa	C10	96.9 (5)
C6	Oa	C8	97.7 (4)
C6	Oa	C9	163.1 (4)
C6	Oa	C10	93.0 (5)
C8	Oa	C9	96.8 (4)
C8	Oa	C10	98.1 (5)
C9	Oa	C10	93.6 (6)
Oa	C8	O8	172.9 (10)
Oa	C9	O9	178.0 (10)
Oa	C10	O10	178.8 (13)

*In degrees. Numbers in parentheses are estimated standard deviations in the least significant digit.

pyramidal geometry with two carbonyl ligands and the two olefinic bonds of the diene unit occupying two coordination positions in the basal plane, and the apical CO bond protruding above the allylic fraction of the seven-membered ring. The Os-C(O) bonds are all close to 1.89 Å. There is apparently no interaction between the Rh centre and the diene carbons with interatomic distances varying between 2.91 (C3) and 2.97 (C5) Å. The torsional angles (ϕ)⁶ between the two π -systems are ca. 60°. As the



ability for $p\pi$ - $p\pi$ overlap varies with $\cos\phi$ ($= 0.5$) this means that conjugation between the allylic and diene fragments is possible. The likelihood of this possibility is diminished however by the long bonds separating the two systems. The Rh to terminal allylic carbon bond lengths are 2.189 (8) (C2) and 2.209 (9) (C7) Å. The bond to the central carbon (C1) is shorter at 2.151 (8) Å. Thus, the Rh-C (diene) bond lengths which are between 2.137 (9) (C12) and 2.159 (9) (C16) are on average shorter than the Rh-C (C₇H₇) bond lengths.

4.2.3. Solid State Structure of 2b.

Orange X-ray quality crystals of **2b** were grown by slow evaporation of a benzene solution of **2b**. Again, the structure was solved by Dr. B. D. Santarsiero of the Structure Determination Laboratory of this department.

The molecular structure and numbering scheme is given in Figure 4.3. Selected bond lengths and angles are given in Tables 4.3 and 4.4. In contrast to **2a**, the C₇H₇ ring in the cis complex, **2b** adopts the boat conformation. This conformation allows a single metal-metal bond to be formed between Os and Rh. This bond is relatively long at 2.89 Å. In the analogous FeRh^{3b} and RuRh⁷ structures, the metal-metal bond lengths were 2.86 and 2.89 Å respectively, indicating the bond length is more a function of the surrounding ligands than on the nature of the metal. The Os-Rh distance can be compared with those in (μ-H₄)Cp^{*}RhOs₃(CO)₉ which vary from 2.74 (unbridged) to 2.91 (μ-H) Å in a tetrahedral RhOs₃ unit⁸. In addition, in the dinuclear coordinatively unsaturated complex Cl₂Os(μ-CO)₂(μ-dppm)₂RhBr the Os-Rh separation is 2.76 Å⁹. Despite the different conformation, the C-C distances within the seven-membered ring maintain the same features as in the trans complex. Thus, the outer diene C-C bonds at 1.423 (10) Å are marginally longer than the central diene C-C bond [1.401 (11)]. This difference (0.02 Å) is not as pronounced as in the trans complex **2a** (0.06 Å) which may be explained by a larger metal-ligand backbonding component from the Os centre in **2a** contrary to a Rh centre in **2b**¹⁰. The largest C-C separation of the C₇H₇ ring is between the diene and allylic fragments [1.464 (10) Å]. This separation is slightly smaller than in the trans complex [ave 1.503 (14) Å]. This, and the smaller torsional angle separating the allyl and diene π-systems of the seven-membered ring (20.6°), implies that there is an increase in conjugation of the allyl and diene parts of the seven-membered ring in the cis complex (**2b**).

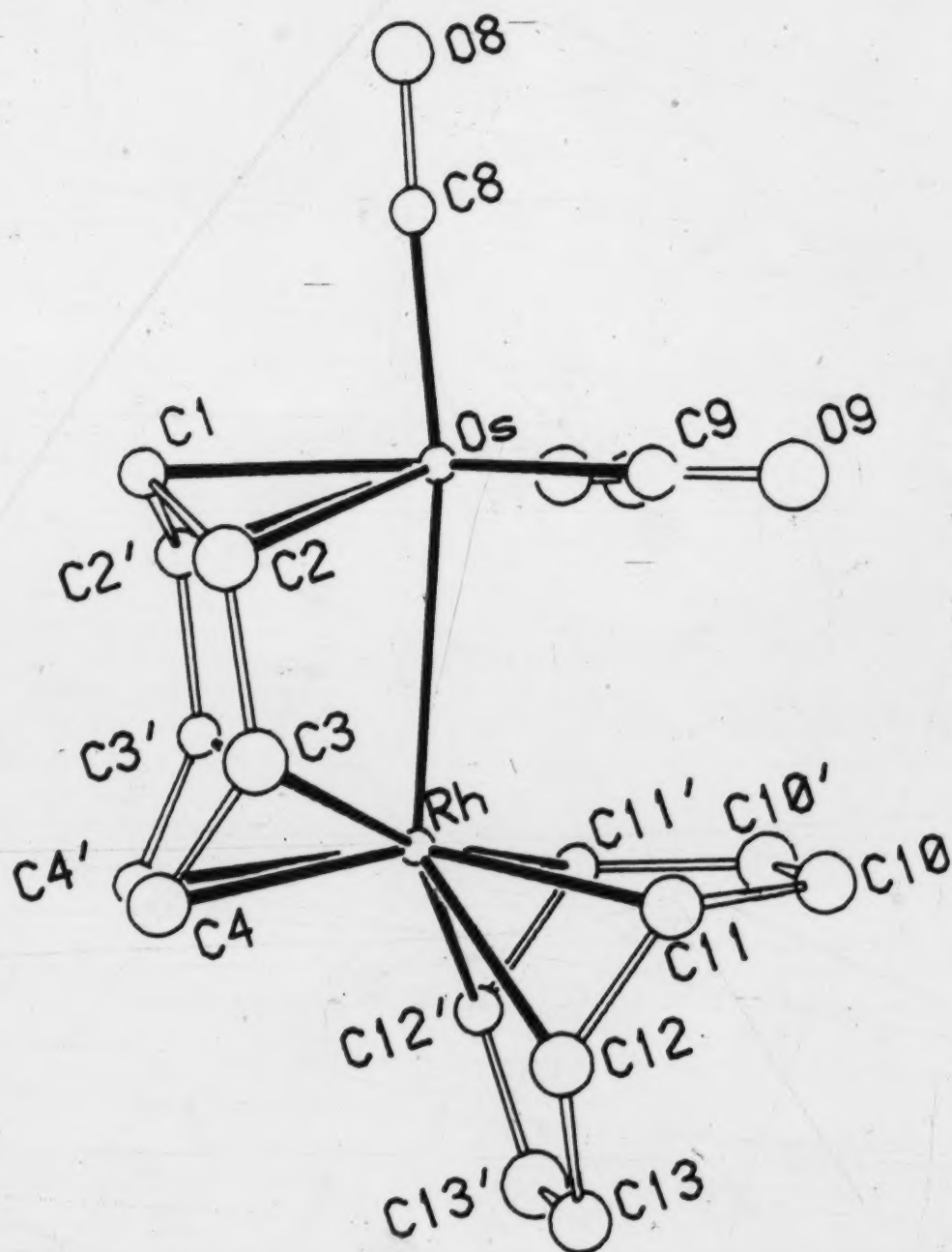


Figure 4.3. Molecular Structure of 2b.

Table 4.3. Selected Interatomic Distances in 2b.

Atom1	Atom2	Length
Os	C1	2.209 (12)
Os	C2	2.278 (8)
Os	C8	1.878 (11)
Os	C9	1.884 (8)
Rh	C3	2.205 (7)
Rh	C4	2.179 (7)
Rh	C11	2.185 (8)
Rh	C12	2.184 (8)
C8	O8	1.146 (14)
C9	O9	1.150 (11)
C1	C2	1.438 (10)
C2	C3	1.464 (10)
C3	C4	1.423 (10)
C4	C4'	1.401 (11)
C10	C10'	1.493 (14)
C10	C11	1.533 (12)
C11	C12	1.392 (11)
C12	C13	1.505 (12)
C13	C13'	1.408 (15)

*In Angstroms. Numbers in parentheses are estimated standard deviations in the least significant digit.

Table 4.4. Selected Interatomic Angles in 2b.^a

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C1	Os	C8	86.9 (4)	C1	Os	C9	134.1 (44)
C1	Os	C2	37.3 (39)	C2	Os	C8	103.3 (3)
C2	Os	C9	157.3 (3)	C8	Os	C9	95.9 (3)
C9	Os	C9'	91.3 (3)	C3	Rh	C4	37.8(3)
C3	Rh	C3'	82.1 (3)	C3	Rh	C4'	68.5 (3)
C3	Rh	C11	96.8 (3)	C3	Rh	C12	93.0 (3)
C3	Rh	C11'	168.4 (3)	C3	Rh	C12'	154.1 (3)
C4	Rh	C4'	37.6 (3)	C4	Rh	C11	117.5 (3)
C4	Rh	C12	92.4 (3)	C4	Rh	C11'	151.7 (3)
C4	Rh	C12'	116.9 (3)	C11	Rh	C12	37.3 (3)
C11	Rh	C11'	82.0 (3)	C11	Rh	C12'	92.9 (3)
C12	Rh	C12'	80.4 (3)	Os	C1	C2	73.5(4)
Os	C2	C1	69.3 (4)	Os	C2	C3	106.6 (4)
Os	C8	O8	179.4(13)	Os	C9	O9	177.9 (8)
Rh	C3	C2	108.7 (4)	Rh	C3	C4	70.1 (4)
Rh	C4	C3	72.1 (5)	Rh	C4	C4'	71.2 (4)
Rh	C11	C10	111.4 (5)	Rh	C11	C12	71.4 (4)
Rh	C12	C11	71.3 (4)	Rh	C12	C13	110.7 (6)
C10'	C10	C11	116.4 (5)	C10	C11	C12	123.8 (7)
C11	C12	C13	123.7 (8)	C12	C13	C13'	118.0 (10)
C2'	C1	C2	117.0 (7)	C1	C2	C3	125.3 (7)
C2	C3	C4	127.9 (7)	C3	C4	C4'	121.8 (9)

^a In degrees. Numbers in parentheses are estimated standard deviations in the least significant digit. Atoms marked with a prime (i.e. C2') related to original atom (i.e. C2) by a mirror plane.

The allylic C-C bond lengths at 1.438 (10) Å are longer as a consequence of being coordinated to a saturated Os centre in **2b**, contrary to an unsaturated Rh centre in **2a** [1.397 (13)]. The Os-C bond distances to the allylic functionality at 2.209 (12) (C1) and 2.278 (6) (C2) Å are on average 0.06 Å longer than to the Rh centre. However, this is compensated for by the average diene (C₇H₇) to metal bond lengths which decrease by ca. 0.05 Å upon replacement of Os (in **2a**) by Rh (in **2b**). All eight Rh-C distances are close to 2.19 Å, with the Rh-outer diene (C₇H₇) separation [2.205 (7)] being marginally longer than the Rh-inner diene (C₇H₇) separation [2.179 (7) Å]. The Os-C(O) bond lengths are again approximately identical at 1.88 Å.

4.2.4. Reaction of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$.

The potassium salt of anion **1c** $[\text{K}(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ also reacts rapidly with $[\text{Ir}(\text{COD})\text{Cl}]_2$ at -78 °C. At the end of the addition, the IR spectrum of the cold THF solution shows three bands at 2059, 1980, 1975 cm⁻¹. These bands are very close to what has already been observed for $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ and the trans OsRh complex **2a** in THF. Hence, it is thought these bands are due to the complex, *trans*-(μ-C₇H₇)Os(CO)₃Ir(COD) (**3a**). However upon solvent removal and extraction in hexane, no evidence of **3a** was obtained and instead a small amount (5%) of the cis isomer (**3b**) was obtained. This may not be totally surprising as the sixteen electron allyl iridium complex, (COD)Ir(η³-C₃H₅) has been obtained at -78 °C and used as an intermediate¹¹. In contrast to the Rh analogue, the allyl-Ir complex proved too unstable thermally to be

isolated. This again suggests that the production of *cis* complex **3b** occurs during decomposition of initially formed *trans* complex, **3a**. Similar to the reactivity of the OsRh compound, when the reaction of $[\text{Ph}_4\text{As}][(\text{C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ with $[\text{Ir}(\text{COD})\text{Cl}]_2$ was carried out, the reaction appeared to follow a different path, with a larger yield (15%) of the *cis* complex **3b** being obtained. A small amount of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ was again formed as well. When this reaction was monitored closely, it was observed that at temperatures below -10°C the *trans* product (**3a**) is stable in solution. However, above this temperature the solution becomes a lighter colour and new bands appear in the IR spectrum indicating that there has been isomerization to **3b**. We defer discussion of the NMR spectra which corroborates the *cis* nature of **3b** to a later section in this chapter.

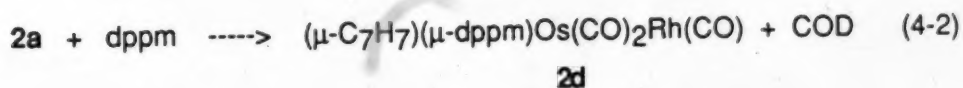
4.2.5. Conversion of **2b** to *cis*-($\mu\text{-C}_7\text{H}_7$)Os(CO)₃Rh(CO)₂, **2c**.

Upon placing a hexane solution of *cis*-($\mu\text{-C}_7\text{H}_7$)Os(CO)₃Rh(COD) (**2b**) under an atmosphere of CO, a reaction occurs slowly at room temperature by substitution of the COD ligand at the Rh centre with two CO ligands. The maximum yield of **2c** is obtained when this reaction is allowed to continue for approximately 2.5 hours. If one allows this reaction to proceed for longer periods of time such that all of the starting material is consumed, decomposition of the product occurs and bands thought to be due to Os(CO)₅ and Os₃(CO)₁₂ appear in the IR spectrum. Upon stopping the reaction after 2.5 hours, fractional crystallization of the residue will give dark red air-sensitive crystals of **2c**. These crystals

sometimes contain trace amounts of **2b** which unfortunately, are difficult to remove. The IR spectrum of **2c**, shows four bands in the carbonyl region at 2063 (s), 2032 (s), 2019 (s), 1980 (m) cm^{-1} , which is very similar to that observed for the analagous RuRh compound [2064 (s), 2023 (s), 2004 (s), 1979 (m) cm^{-1}]. As expected the ^1H and ^{13}C NMR spectra show only one signal for the C_7H_7 ligand. In the room temperature ^{13}C NMR spectrum there are two additional resonances for the $\text{Os}(\text{CO})_3$ (δ 176.7) and $\text{Rh}(\text{CO})_2$ (δ 193.0) groups.

4.2.6. Reaction of *trans*-(μ - C_7H_7) $\text{Os}(\text{CO})_3\text{Rh}(\text{COD})$ (**2a**) with dppm.

In contrast to the slow reaction of **2b** with CO and the generally slow reactions of the cis compounds (μ - C_7H_7) $\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ with phosphines (see Chapter 2), the trans complex **2a** was observed to react rapidly with dppm at room temperature. This leads to substitution of the COD ligand and isomerization to a cis compound, **2d**. The rapid reactivity is presumably due to the coordinative unsaturation which is present at the Rh centre.



This reaction is most cleanly carried out by slow addition of a solution of **2a** to dppm. We propose that this minimises the risk of addition products containing one dppm ligand bridging two different Rh centres as the rapid reaction continually ensures a low concentration of **2a**. Complex

2d is a dark red, air sensitive compound sparingly soluble in hexane. The IR spectrum in the carbonyl region shows three bands at 1974 (s), 1937 (s), 1894 (m) cm^{-1} , which suggests the presence of a metal-metal bond bridged by dppm, by comparison with the precedential RuRh compound (1975 (s), 1949 (s), 1904 (br) cm^{-1})¹². The ^{31}P NMR spectrum (Figure 4.4) which has two signals, only one with Rh coupling, clearly confirms this assignment. The room temperature ^1H and ^{13}C NMR spectra show evidence for the expected ring whizzing of the C_7H_7 ligand, but also show that the two methylene protons of the dppm ligand are undergoing exchange. The latter fluxional process, which involves the dppm ligand, will be commented upon more fully in the discussion. At 0 °C (Figure 4.4) the expected ^1H NMR spectrum is observed.

4.2.7. Fluxional Behaviour of Isomeric (μ - C_7H_7) $\text{Os}(\text{CO})_3\text{M}'(\text{COD})$ Complexes ($\text{M}' = \text{Rh}, \text{Ir}$).

The variable temperature ^1H NMR spectra of **2a** and **2b** are shown in Figures 4.5 and 4.6 respectively. Simulation of the observed spectra for **2b** allowed rate constants for the 1,2 shift process to be estimated, and these are also shown in Figure 4.6. These calculations are discussed in more detail later in this chapter and in Chapter 7. As can be seen from Figures 4.5 and 4.6, the room temperature ^1H NMR spectra of both OsRh complexes show a single peak for the C_7H_7 ligand due to rapid metal migration around the seven-membered ring, as well as peaks due to the COD ligand. For **2b**, a sharp singlet is seen for the C_7H_7 ligand at δ 3.7.

Figure 4-4. Low Temperature (0 °C) ^1H (a) and ^{31}P (b) NMR Spectra for 2d.

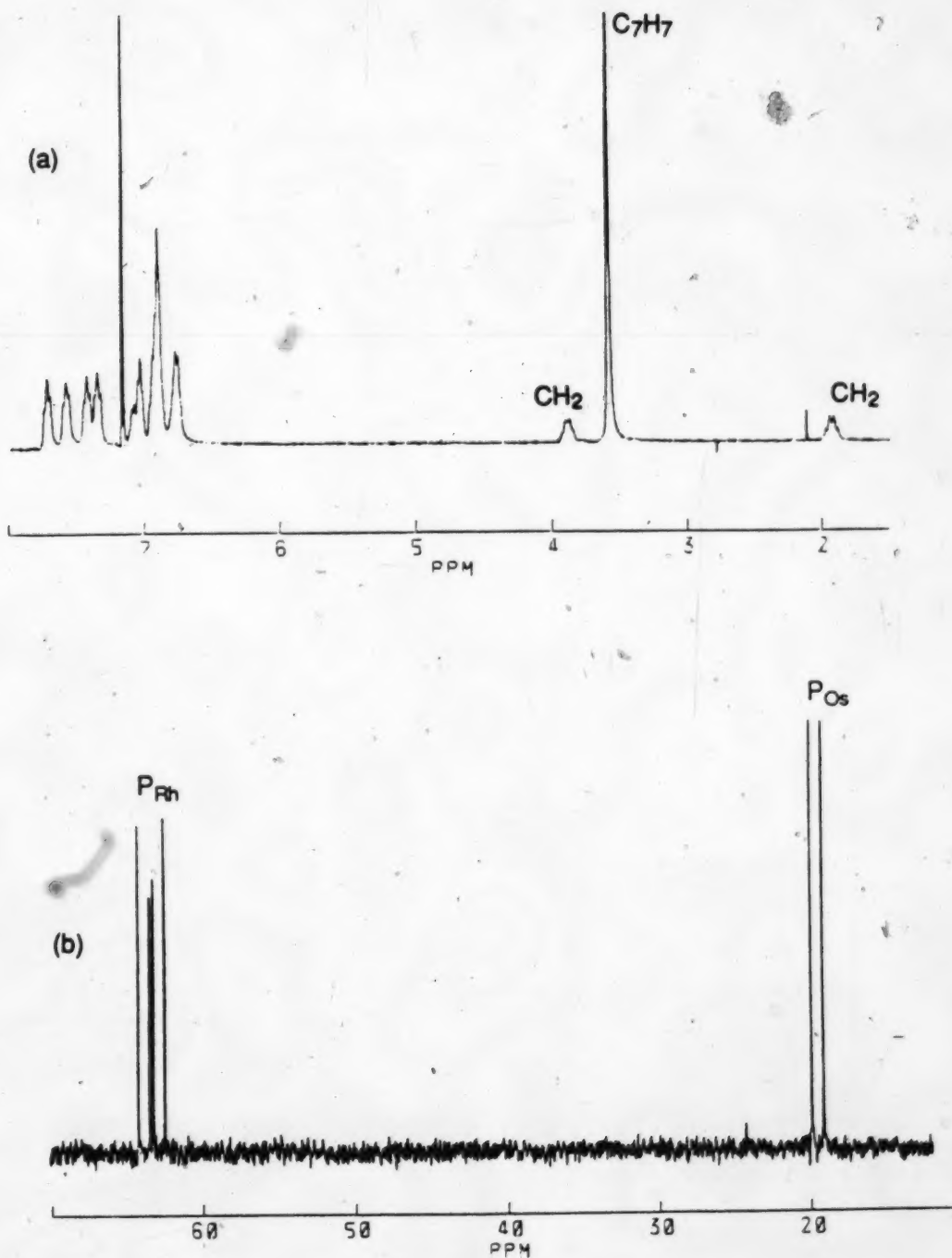


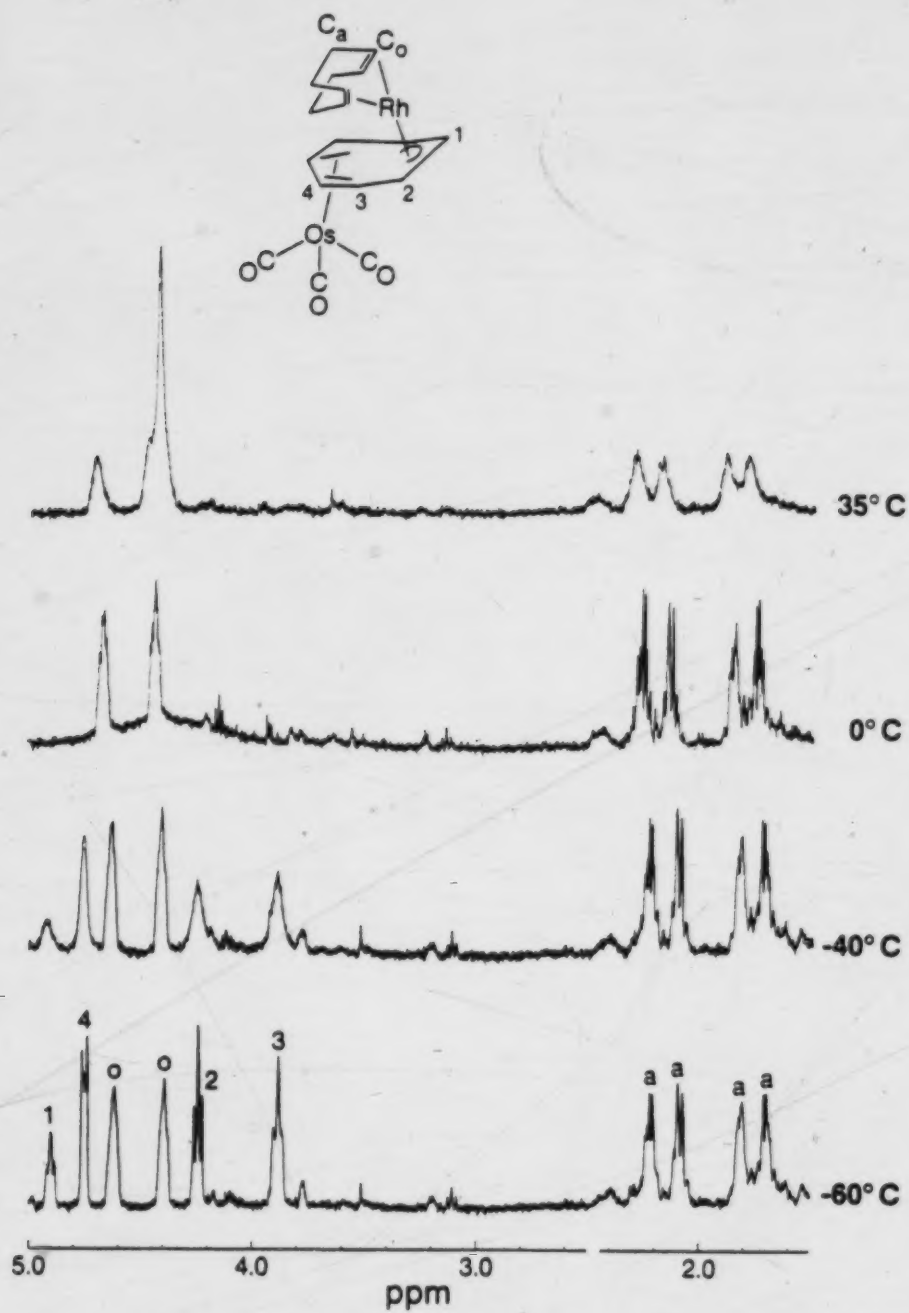
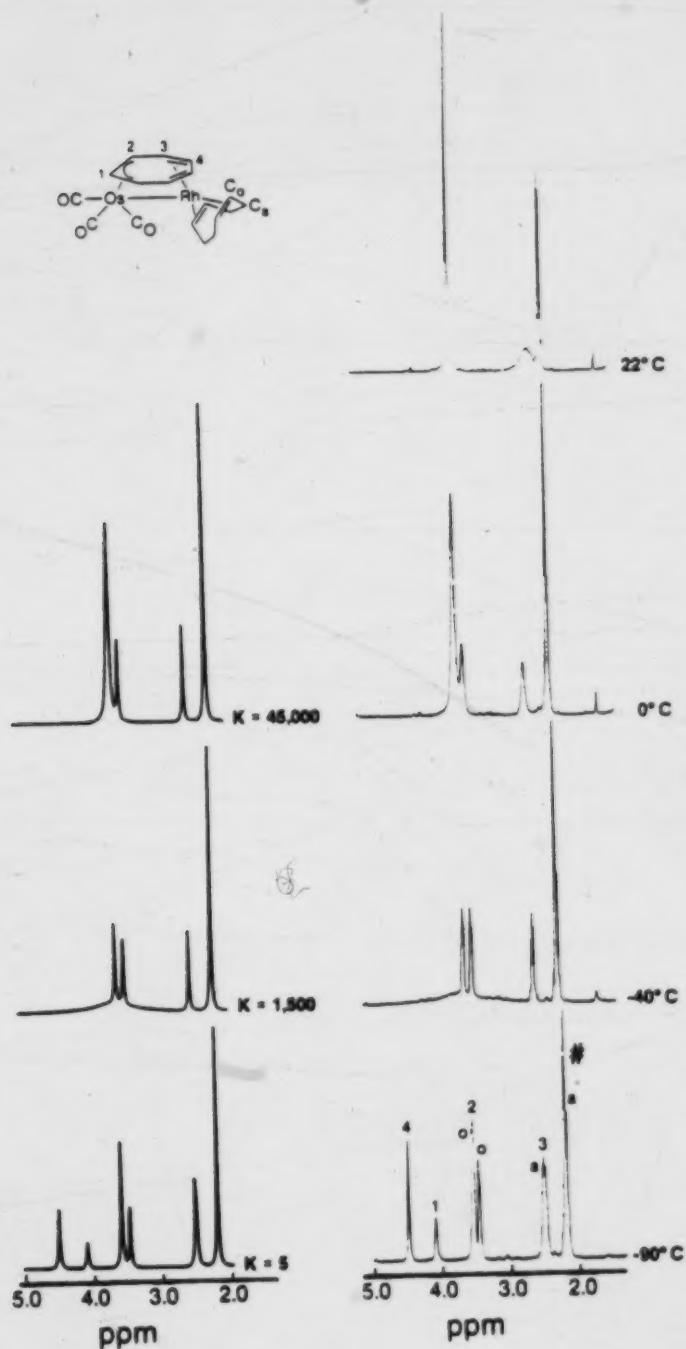
Figure 4.5. Variable Temperature ^1H NMR Spectra for 2a.

Figure 4-6. Observed and Simulated Variable Temperature ^1H NMR Spectra for 2b. # = toluene solvent

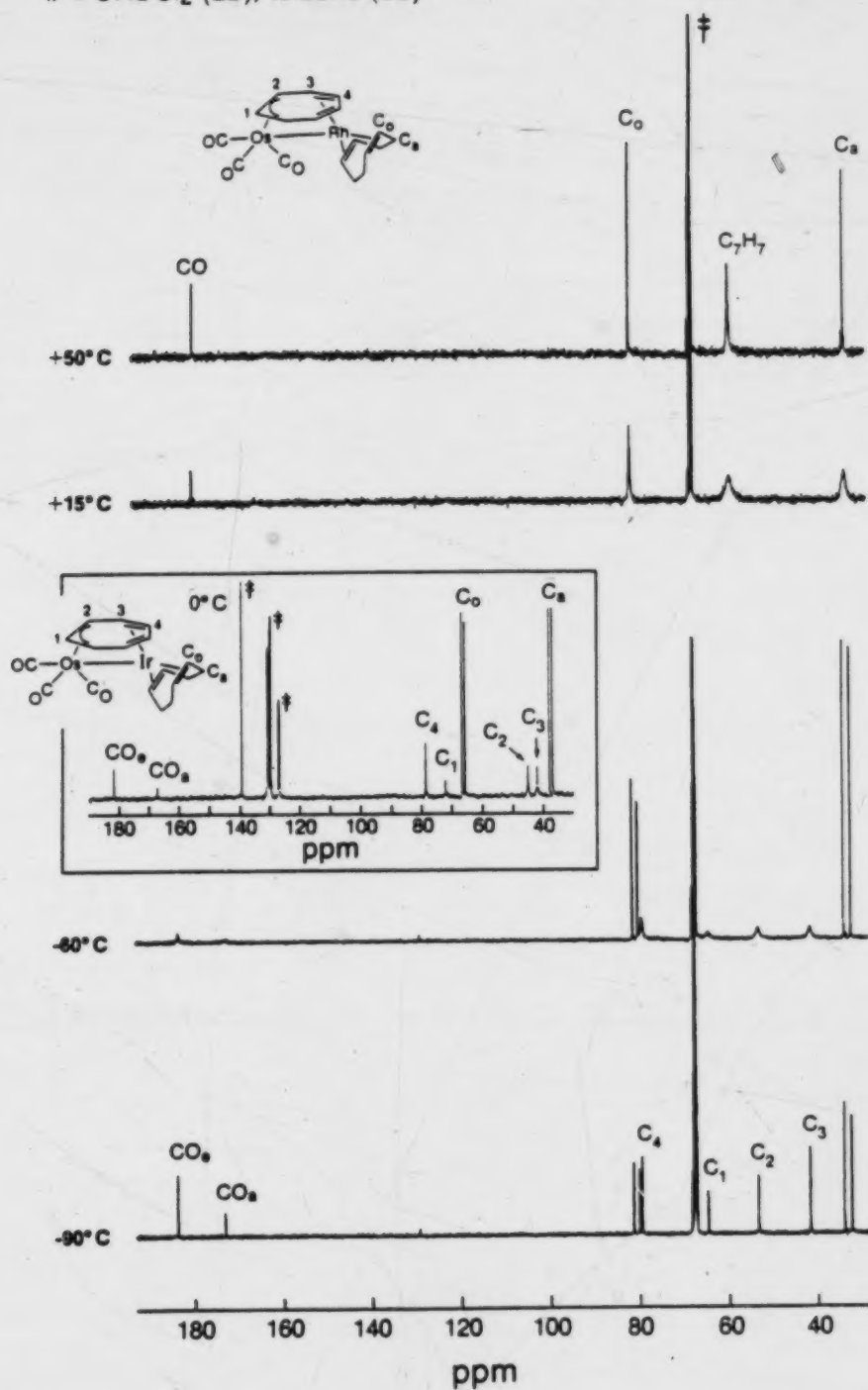


This is superimposed upon a broad singlet due to the olefinic hydrogens of the COD ligand. There is an additional broad singlet at δ 2.5 due to four of the aliphatic hydrogens of the COD ligand, and a sharp multiplet at δ 2.3, also of intensity four, for the remaining four aliphatic hydrogens. The signals of intensity four can be explained by invoking a rotation (about the metal-ligand axis) of the COD ligand which would lead to three peaks (all intensity four) for the olefinic, and inner and outer aliphatic hydrogens of the COD ligand. The broad nature of two of the signals is a result of the ligand rotation beginning to slow down at this temperature. Upon cooling to 0 °C, there are four peaks of intensity ratio 9:2:2:6. The peak of intensity 9 at δ 3.7 corresponds to the cycloheptatrienyl ring and two olefinic hydrogens. This signal is not as sharp as at room temperature due to the onset of the freezing out of metal migration around the C₇H₇ ring. The adjacent signal at δ 3.5 is due to the remaining two olefinic hydrogens of the COD ligand. In the low temperature limiting spectrum, four resonances of intensity 2 are expected for the eight aliphatic hydrogens of the diene ligand, however three of these signals overlap which explains the two high field signals of intensity 2 and 6. At -40 °C only a very broad hump for the C₇H₇ ring is observed, which makes the COD signals easily visible in intensity ratio 2:2:2:6. Upon further cooling to -90 °C, almost complete stoppage of the metal migration around the cycloheptatrienyl ring is observed. Unfortunately at this temperature there are no observable H-H couplings and there is also overlap of the terminal allylic and outer diene hydrogens of the C₇H₇ moiety with signals due to the COD ligand. However the inner diene (H4) and central allylic hydrogen (H1)

resonances are well separated at lower field. Consequently, for this compound, assignments of the ring hydrogens were based on the characteristic high field shift of the outer diene protons, low field shift of the inner diene protons¹³, and the different intensity of H₁. Comparison with **3b**, whose assignment is based on decoupling experiments, further strengthens this proposal.

The variable temperature ¹³C NMR spectra are shown in Figure 4.7. The low temperature ¹³C NMR spectrum at -90 °C gives the expected signals for the static C₇H₇ ring and COD ligand. Additionally there are also two resonances in the CO region indicating that the fluxional process interconverting the three CO groups at room temperature has also been stopped. However upon warming to -60 °C both broadening of the CO and C₇H₇ resonances has begun. The relationship between the carbonyl scrambling process and the motion of the seven-membered ring is further commented upon in the discussion.

For the trans compound, **2a**, the variable temperature NMR results proved to be different, showing decreased fluxional behaviour at ambient temperature. This is consistent with the trans assignment^{13b}. In the ¹H NMR spectrum at +35 °C, the signal for the C₇H₇ ring is already broad and there are six signals for the COD ligand indicating almost complete freezing out of rotation of this moiety. At 0 °C, there is only a very broad resonance for the C₇H₇ ring and the signals for the COD ligand are readily distinguished. The slow limiting spectrum is observed at -60 °C,

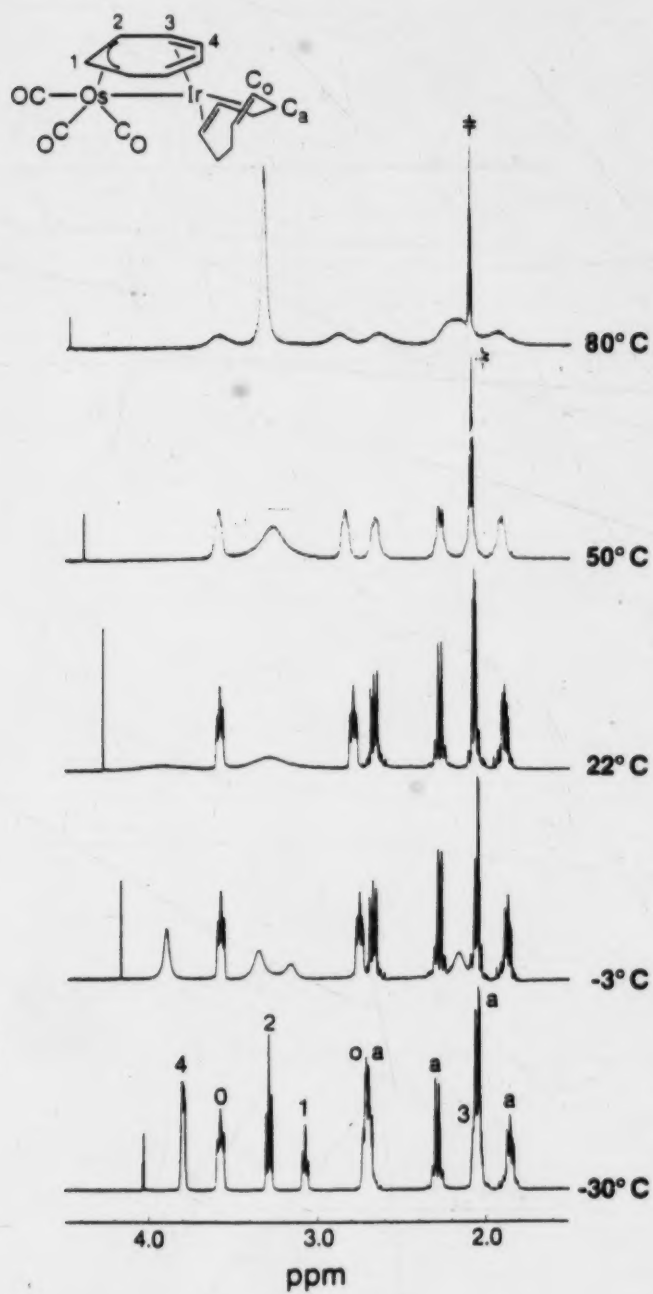
Figure 4.7. Variable Temperature ^{13}C NMR Spectra for 2b (and 3b).# = CH_2Cl_2 (2b), toluene (3b)

and fortunately, none of the resonances overlap. At this point there are ten signals, one of which has intensity 1, and the others all have intensity 2. Clearly the signal of intensity 1 is due to the central allylic ring hydrogen. In contrast to *cis* compound **2b**, this is the lowest field resonance for **2a**. Assignments of the other C₇H₇ ring signals were made from homonuclear decoupling experiments. Again, in the ¹³C NMR spectra the low temperature limiting spectrum shows two signals in intensity ratio 2:1 for the CO groups on Os. However, upon warming the sample from -45 °C to room temperature CO exchange is observed, and at room temperature only one carbonyl signal is observed. Unfortunately, no Rh coupling was observed to any of the cycloheptatrienyl carbons in the low temperature limiting spectrum due to the limited solubility of **2b**, and also the small magnitude of the couplings involved.

In the OsIr compound **3b**, a further decrease in fluxional behaviour is observed (Figure 4.8). In the ¹H NMR spectrum at room temperature six signals for the static COD ligand are seen and the C₇H₇ ring signal consists of two broad peaks. The slow limiting spectrum is obtained already at -30 °C. Unambiguous assignments of the ring hydrogens were again accomplished by decoupling experiments. The sample had to be heated to 80 °C to obtain a fairly sharp singlet for the C₇H₇ ring and to see the first signs of COD rotation. Again as evidenced from the variable temperature ¹³C NMR spectra (see inset in Figure 4.7) onset of the carbonyl scrambling and ring rotation processes occur at about the same temperature (0 °C).

Figure 4.8. Variable Temperature ^1H NMR Spectra of 3b.

= toluene solvent



4.3. Discussion.

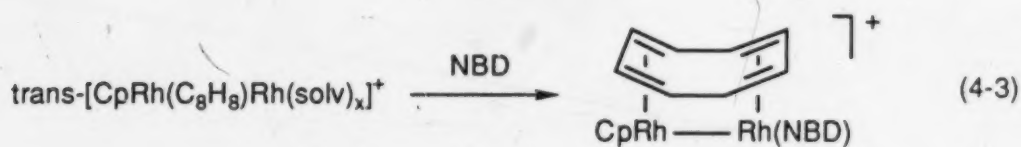
4.3.1. Synthetic Aspects.

As has already been mentioned, the reaction of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ (**1c**) with $[\text{Rh}(\text{COD})\text{Cl}]_2$ leads preferentially to the trans compound **2a** as the kinetic product. A similar reaction occurs with the related Ir complex however the trans OsIr compound proved to be too thermally unstable to isolate. The reactivity of **1c** observed here is thus in contrast to the previously reported reactivity of the related Fe and Ru anions (**1a** and **1b**) where no evidence of a trans intermediate was seen in the synthesis of the corresponding $\text{MRh}^{3\text{a,b}}$ and $\text{Mlr}^{3\text{c,d}}$ compounds. It seems unlikely that in these reactions the trans complex could be formed and converted to the cis complex rapidly enough at -78°C to avoid detection. This differing reactivity suggests an inherent difference in the electronic structure of the mononuclear anionic complexes. In order to pursue any evident differences between the anionic complexes as the metal is changed, the crystal structures and ^1H and ^{13}C NMR variable temperature spectra of the Ru and Os anions (**1b** and **1c**) have been investigated. The results of these studies are reported in the next chapter.

An additional noteworthy feature of these reactions is that a small amount of $(\eta^4\text{-C}_7\text{H}_8)\text{Os}(\text{CO})_3$ is invariably obtained in most syntheses of **2a** and **2b**. This could be a result of some residual HO^tBu acting as a reprotonating agent in a reaction with the anionic osmium complex **1c**.

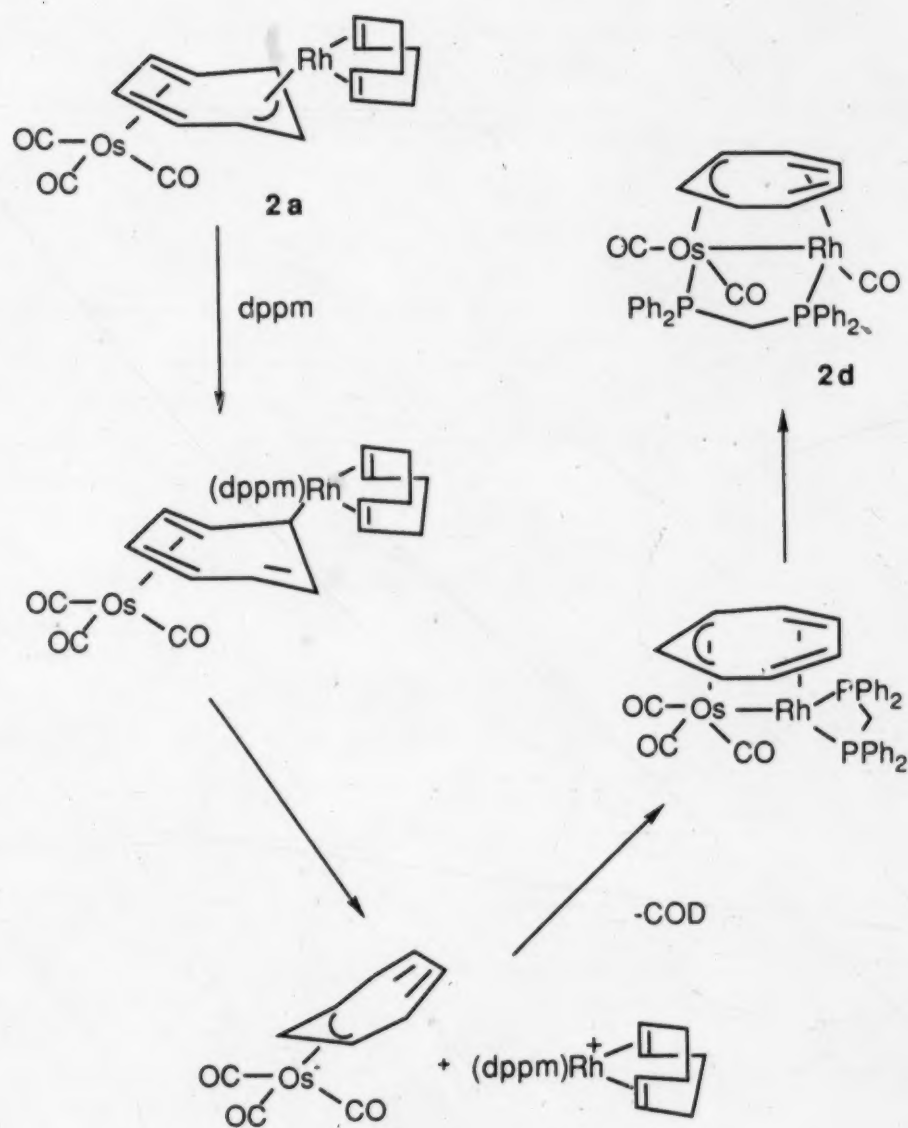
Alternatively this could result from hydrogen abstraction from the COD ligand. The latter possibility has been observed before, for instance, reaction of ethyl lithium with $[\text{Rh}(\text{COD})\text{Cl}]_2$ yields $[\text{Rh}(\text{COD})(\text{i-C}_2\text{H}_5)]_2$ which subsequently decomposes to the cluster $[\text{HRh}(\text{C}_8\text{H}_{11})]_4^{14}$.

The stable and coordinatively saturated cis compounds **2b** and **3b**, are the thermodynamic products of these reactions and appear to be formed by isomerization of their trans isomers. This process occurs most cleanly in the presence of added chloride. Trans to cis isomerization in a cyclooctatetraene bridged dinuclear Rh complex (shown below) has been reported previously in acetone or CH_2Cl_2 solution¹⁵:



An even more efficient means of producing a cis complex from **2a** is the reaction with dppm. The most likely explanation for the trans to cis rearrangement in this reaction is that one end of the diphosphine will coordinate first to the unsaturated Rh centre and then $\text{Rh}(\text{COD})(\text{dppm})^+$ will dissociate from the C_7H_7 ligand in order to attack the same or a different molecule from the other side of the seven-membered ring (Scheme 4.2). The driving force for the isomerization is the formation of two eighteen electron metal centres.

Scheme 4.2. Proposed Formation of 2d.



The first step in this scheme is likely when one considers the precedential rapid reactivity of (allyl)Rh(COD) with phosphines¹⁶. Additionally, there are some known complexes closely related to the mononuclear cationic Rh intermediate proposed in the scheme. These compounds of formula (diphosphine)Rh(diene)⁺ are known to dissociate the diene in polar solvents and to act as olefin hydrogenation and isomerization catalysts in solution¹⁷. Considering these facts, it seems very plausible that Rh(dppm)(COD)⁺ could easily dissociate from the C₇H₇ ring, and that subsequent formation of a cis complex with loss of COD is also highly feasible. The chelating *cis*-(μ-C₇H₇)Fe(CO)₃Rh(dppm) complex is known to convert to its dppm bridged isomer^{3a}; however, the corresponding chelating RuRh compound has remained elusive (despite attempts at observation)^{7,12}.

4.3.2. Fluxional Behaviour of *cis*-C₇H₇ Bridged Compounds, 2b, 2d, and 3b.

Prior to this work, an expected feature of *cis*-cycloheptatrienyl bridged bimetallic complexes has been that rapid rotation of the cycloheptatrienyl ring will occur on the NMR timescale at all temperatures. In contrast with this, freezing out of the C₇H₇ ring motion at an accessible temperature has been taken as indicative of a *trans* arrangement^{13b}. In this work we have shown that in isomeric *cis* and *trans* complexes the activation barrier for C₇H₇ rotation is indeed larger for the *trans* compound (2a) than for the *cis* isomer (2b); however, freezing out of metal migration around the seven-membered ring in the *cis* complex at low temperature has also been

observed. This is unusual for *cis* C₇H₇ bridged complexes but has been observed before for the analogous RuIr compound (see Chapter 2) at the same temperature (-100 °C) and is presumably due to the requirement of having a second and a third row transition element involved in bonding to the ring. In continuing this trend, the low temperature limiting spectrum for the third row combination, **3b** was obtained at - 30 °C. One exception to this trend is provided by the unrelated hydrido CoCr complex, Cp⁺Co(μ-η³-η⁴-C₇H₇)(μ-H)Cr(CO)₃¹⁸, in which, rotation of the cycloheptatrienyl ligand has also been stopped. These trends will be discussed further in Chapter 7.

Spin inversion experiments have been carried out on both **2a** and **3b**. For both compounds it was determined that the ring was rotating by a series of intramolecular 1,2 shifts, a process common in organometallic systems and the only process elucidated for η³-C₇H₇ systems^{5,19}. From these experiments, the free energies of activation were found to be 12.0 and 13.8 kcal mole⁻¹ for **2a** and **3b** respectively. Simulation of the variable temperature ¹H NMR spectra of **2b** (see Figure 4.6) at seven temperatures yielded an activation energy of 10 kcal mole⁻¹ for the same process in the *cis* OsRh complex (**2b**). The calculated and observed rate constants, and activation parameters for the 1,2 shift processes are recorded in Tables 4.5 and 4.6. Not unexpectedly, there is a substantial increase in activation energy upon replacement of Rh with Ir. In contrast with this, there is a surprisingly small difference in activation

Table 4.5. Observed and Calculated Rate Constants for **2a**, **2b** and **3b**^a.

2b (c-OsRh)			2a (t-OsRh)			3b (c-OsIr)		
Temp	Obs	Calc	Temp	Obs	Calc	Temp	Obs	Calc
173	1.0	1.02	201.5	0.86	0.81	236.5	1.04	1.04
183	5.0	4.84	208.5	2.10	2.13	243.5	2.81	2.44
193	20.0	19.55	215.0	5.06	4.95	249.0	4.44	4.58
203	75.0	69.03	221.0	9.16	10.30	255.5	8.52	9.35
233	1500	1605.3	230.0	31.10	28.82	261.5	18.43	17.94
243	3500	3869.7						
273	45000	37144						

a Observed values for **2b** obtained from simulation of NMR data. Observed values for **2a** and **3b** from spin inversion experiments. Calculated values obtained from a non-linear least squares fitting procedure.

Table 4.6. Activation Parameters for C₇H₇ Rotation in Compounds **2a**, **2b** and **3b** (kcal mol⁻¹)^b.

Compound	$\Delta H^\ddagger$	St.D	$\Delta S^\ddagger$	St.D	$\Delta G^\ddagger$	Error ^c
2b (c-OsRh)	9.43	0.53	-2.92	2.37	10.3	1
2a (t-OsRh)	11.10	1.75	-3.06	8.25	12.0	2
3b (c-OsIr)	13.36	0.91	-1.51	3.73	13.8	4

b Activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated from the rate constants using a non-linear least squares fitting procedure. Units for $\Delta S^\ddagger$ are cal/mole K.

c Errors calculated by summation of one standard deviation for $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

energy between the cis and trans OsRh complexes considering the large difference in structure. Further inferences as to the nature of these differences were sought from the two other fluxional processes occurring in these molecules, i.e. COD rotation and carbonyl group exchange. The rate constants for these processes were approximated at the coalescence temperature²⁰ in order to obtain the respective approximate free energies of activation. These results are summarised in Table 4.7.

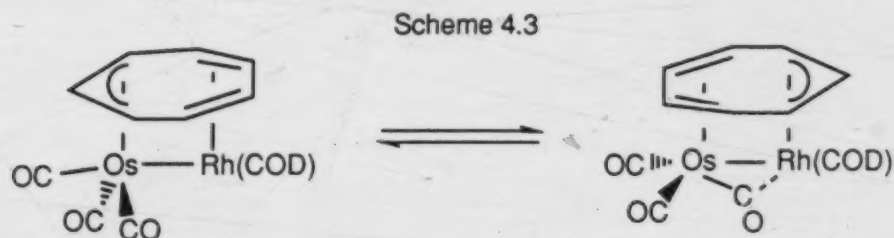
Table 4.7. Summary of Activation Parameters for the Fluxional processes Occuring in $(\mu\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{M}'(\text{COD})$ compounds ($\text{M}' = \text{Rh}, \text{Ir}$)^a.

Compound	COD		Os(CO) ₃		C ₇ H ₇	
	T _c /°C	ΔG [‡]	T _c /°C	ΔG [‡]	ΔG [‡]	Error
3b (c-OsIr)	95 ^b	18	60	14.3	13.8	2
2b (c-OsRh)	15 ^c	14	-30	10.5	10.3	1
2a (t-OsRh)	-	-	-10	12.3	12.0	4

a. ΔG[‡] in units of kcal mole⁻¹. Errors in ΔG[‡] for COD and Os(CO)₃ fluxional processes approximately 1 kcal mole⁻¹. b. Calculated from coalescence of aliphatic hydrogen resonances. c. Calculated from coalescence of olefinic carbon resonances.

One striking result from the table is that for all three compounds studied in this report, the activation energy for C₇H₇ rotation and CO exchange are

equivalent within experimental error. Thus for the two *cis* compounds, **2b** and **3b**, the free energies of activation for CO exchange are approximately 10 and 14 kcal/mole respectively. This is a very large difference upon replacing the distant Rh centre with an Ir centre and hence implies that there is more than just a spectator role for the second metal. This can be explained by invoking an intermediate in this process which contains a semibridging carbonyl ligand and a reversed $\mu\text{-}\eta^4\text{-}\eta^3\text{-}$ bonding mode of the seven-membered ring²¹. This intermediate, which has a trigonal prismatic geometry at Os, therefore accomplishes both ring rotation and carbonyl group exchange as shown in Scheme 4.3, and hence accounts for the same free energy of activation for both processes.



A different form of fluxional behaviour was seen for the bridging dppm complex. This is a process that has previously been observed in the analogous RuRh compound^{7,12} and is due to a "tandem berry pseudo-rotation" of the two metals. This causes movement of the dppm ligand directly underneath the seven-membered ring creating a mirror plane (Scheme 4.4).

Scheme 4.4

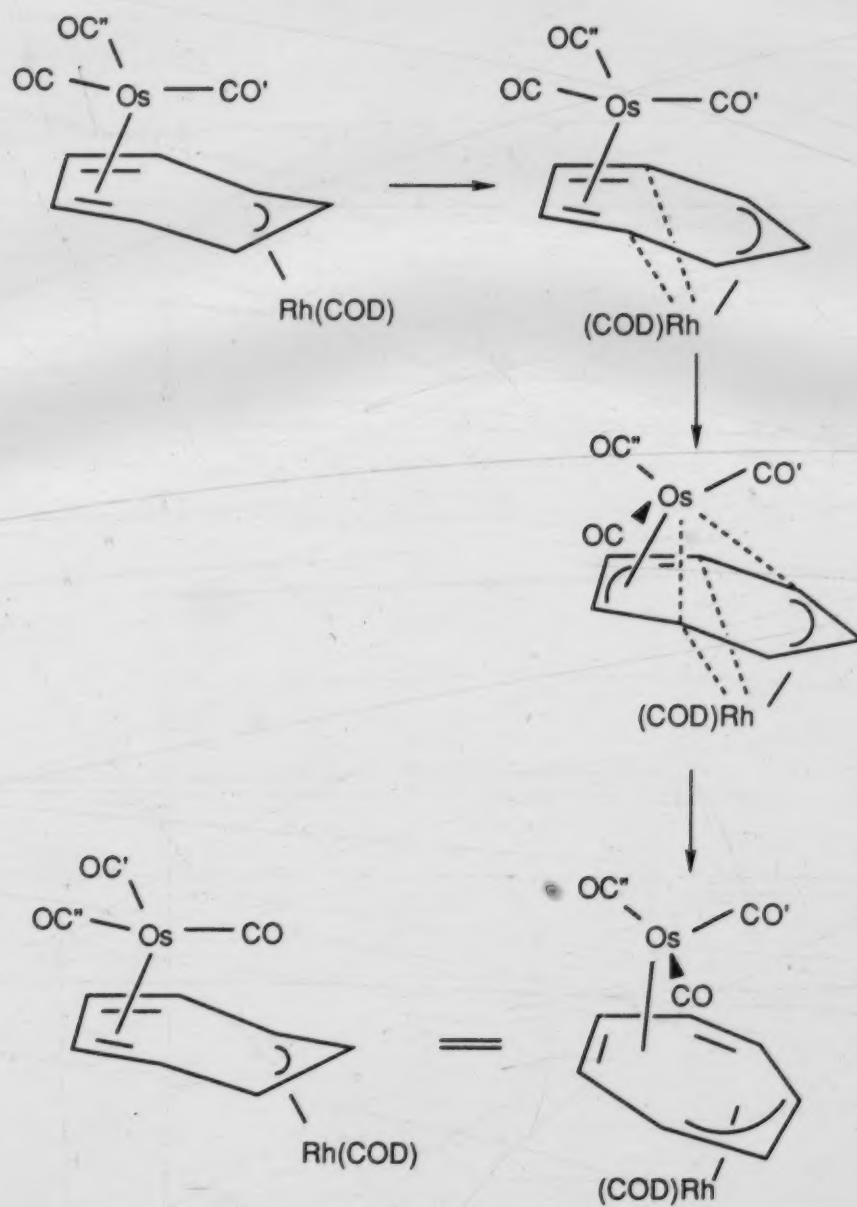


In the lower temperature spectrum, recorded at 0 °C, the dpmm ligand is static as evidenced by the two diastereomeric methylene signals of the dpmm ligand and the four distinct ortho resonances. The same phenomenon is observed in the ^{13}C NMR spectrum such that the two CO groups on Os are exchanging at room temperature. The seven-membered ring however, is still rotating rapidly giving a sharp singlet.

4.3.3. Fluxional Behaviour in *trans*-($\mu\text{-C}_7\text{H}_7$)Os(CO) $_3$ Rh(COD) (**2a**).

As has been stated earlier, metal migration around the C_7H_7 ligand requires a higher energy in **2a** than in **2b**. Interestingly, rotation of the COD ligand, bound only to Rh also occurs for **2b** but not for **2a** at room temperature. This implies that this ligand also has a stronger interaction in trans complex, **2a**. In this case also, the carbonyl scrambling and ring rotation processes in **2a** appear to be degenerate. However in contrast to

Scheme 4.5. 1,2-metal shift of the C_7H_7 ligand with respect to Os and Rh.



the synergic motion of the Os centre, the Rh(COD) group slides in the opposite direction *without* any accompanying ligand movement. Rotation of the tightly bound COD group begins only above 35 °C. One possible pathway for the 1,2 slide motion of the Rh(COD) group could involve an interaction of Rh with the outer diene carbons bonded to Os (see Scheme 4.5). This would provide a low energy intermediate available to **2b** for this process. The sort of 3-centre 2-electron bonding required for this low energy intermediate has been observed several times previously to coordinatively unsaturated Rh complexes^{15,22}, including a very closely related complex containing Cr(CO)₃ and Rh(COD) moieties on opposite faces of the indenyl ligand²³. Additionally, it is known that η^3 -pentadienyl "sixteen electron" Rh^I complexes undergo fluxional behaviour and this is thought to occur through an η^5 intermediate²⁴. This process however, involves an open pentadienyl chain and thus involves a 1,3 metal shift with respect to the ligand. A 1,3 shift process also occurs in the dicationic slipped triple decker complex²² CpRh(C₈H₈)RhCp²⁺. Scheme 4.5 also attempts to show how the migration of the Os(CO)₃ moiety may cause degenerate carbonyl scrambling. It is seen that the cog-wheel type motion of the Os(CO)₃ group around the inner perimeter of the seven-membered ring causes the unique carbonyl group to exchange with the other two equivalent CO groups. The type of motion depicted is very similar to that of the Fe(CO)₂L group which has been observed in (η^4 -cyclooctatetraene)Fe(CO)₂(CNPr)²⁵ and which also undergoes degenerate metal shifts and CO exchange.

4.4. Summary

Upon reaction with Rh or Ir based transition metal electrophiles, the preferential site of attack on $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ is at the exo face of the seven-membered ring. This is in contrast to the reactivity with the analogous Fe or Ru anionic complexes. Thus the reaction of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3^-$ with $[\text{Rh}(\text{COD})\text{Cl}]_2$ leads to the formation of *trans*-($\mu\text{-C}_7\text{H}_7$)Os(CO)₃Rh(COD) (**2a**). The *trans* compound (**2a**) reacts rapidly with nucleophiles such as dppm and Cl⁻. The reaction with Cl⁻ leads ultimately to the *cis* heterobimetallic compound, and isomer of **2a**, *cis*-($\mu\text{-C}_7\text{H}_7$)Os(CO)₃Rh(COD) (**2b**). The *trans* isomer **2a** and the *cis* OsIr compound *cis*-($\mu\text{-C}_7\text{H}_7$)Os(CO)₃Ir(COD) (**3b**) were observed to be undergoing fluxional behaviour in which the C₇H₇ ligand undergoes 1,2-metal shifts. For the *trans* OsRh compound **2a**, this motion may be connected to rotation of the Os(CO)₃ group, indicating that the Os centre may have more influence on the energetics of this process. The *cis* OsRh isomer (**2b**) shows increased fluxional behaviour and increased conjugation of the seven-membered ring over the *trans* compound (**2a**). This may be a consequence of the unsaturation present at the Rh centre in **2a**. As a result of these studies, a series of *cis* heterobimetallic complexes ($\mu\text{-C}_7\text{H}_7$)M(CO)₃M'(COD) (M = Fe, Ru, Os; M' = Co, Rh, Ir) within two triads is now close to complete. In these complexes, the global, and the local fluxional behaviour at each metal decreases as one descends either metal triad. This is consistent with the known increase in metal-ligand bond strengths which generally occurs upon descending a transition metal triad²⁶.

4.5. Experimental.

4.5.1. General Techniques and Reagents, Chapter 4.

Bis(diphenylphosphino)methane (DPPM) was purchased from Pressure Chemical Company. Tetraethyl ammonium chloride, cycloheptatriene, bis(triphenylphosphine)iminium chloride (PPNCl), 1,5-cyclooctadiene (COD) and potassium tertiarybutoxide (KO^tBu) were purchased from Aldrich Chemical Company. Cycloheptatriene was distilled prior to use and potassium tertiarybutoxide was sublimed prior to use ($150\text{ }^\circ\text{C}$, 10^{-3} mmHg). All other materials were used as received. Ammonium hexachloroiridate (IV) and hydrated rhodium trichloride were obtained from Johnson Matthey Inc. $[\text{Ir}(\text{COD})\text{Cl}]_2^{27}$ and $[\text{Rh}(\text{COD})\text{Cl}]_2^{28}$ were prepared according to literature methods. Crystallization of **2a**, and the reaction of **2a** with dppm were carried out in a Vacuum Atmospheres Model MO40-2 glove box under purified nitrogen. Mechanistic deductions from variable temperature NMR spectra were from line broadening and selective inversion recovery procedures²⁹. Simulation of the NMR spectra was accomplished in the conventional manner³⁰. Calculation of the activation parameters from the deduced rate constants was accomplished by a non-linear least squares fitting procedure. The complete X-ray solid state structure determinations on compounds **2a** and **2b** were carried out by Dr. B. D. Santarsiero of the Structure Determination Laboratory of this department. A limited amount of pertinent experimental data is extracted from the respective structure reports and included in this thesis for the sake of completeness. Further information including listings of observed

and calculated structure factor amplitudes of all reflections may be obtained from Dr. B. D. Santarsiero or Dr. J. Takats of this department.

4.5.2. Synthesis of *trans*-(μ -C₇H₇)Os(CO)₃Rh(COD), **2a**.

K(C₇H₇)Os(CO)₃ (0.100 g, 0.25 mmoles) was prepared in THF from KO^tBu (0.028 g, 0.25 mmoles) and (η^4 -C₇H₈)Os(CO)₃ (0.090 g, 0.25 mmoles)⁵. The dark red THF solution of the anion was concentrated to 1 ml and added to a suspension of [Rh(COD)Cl]₂ (0.062 g, 0.125 mmoles) in diethyl ether (20 ml) at -78 °C. Most of the suspended solid dissolved to give a pale red solution which was concentrated to ca. 7 ml over 8 hours. Degassed hexane (7 ml) was added slowly to the solution which was allowed to warm to -10 °C. A yellow solution with a yellow-brown precipitate was obtained. The solution was filtered and the residue was extracted twice with hexane (7 ml) at -10 °C. The solvent was removed from the combined extracts to give a yellow solid which was then extracted three times with hexane (1 ml) at room temperature and filtered through celite to give a yellow solution and a dark brown precipitate. The combined filtrates were concentrated and crystallised from CH₂Cl₂/hexane to give after one crystallization 28 mg (20%) of **2a** as a yellow-orange microcrystalline material. Further concentration of the mother liquor gave a further 5 mg of **2a** (23% overall). The residual dark brown precipitate was redissolved in THF. Addition of Et₄NCl (2 mg) caused isomerization of residual **2a** to give **2b** (5 mg). Combined yield of **2a** and **2b**, 26%.

Anal. Calcd. for $C_{18}H_{19}O_3OsRh$: C, 37.50, H, 3.32. Found: C, 37.93, H, 3.59.

Mass Spectrum (70 eV, 160 °C); M^+ , $M^+ - nCO$ ($n = 1 - 3$).

IR (hexane): ν_{CO} 2060(s) 1991(s) 1979(s) cm^{-1} .

^1H NMR (25 °C, CD_2Cl_2): δ 4.70 (m, 2H, CH_{COD}), 4.43

(m, 9H, $C_7H_7 + CH_{COD}$),

2.30 (m, 2H, CH_2_{COD}), 2.18 (m, 2H, CH_2_{COD}), 1.88 (m, 2H, CH_2_{COD}), 1.77

(m, 2H, CH_2_{COD}), (-50 °C): 4.90 (m, 1H, H_1), 4.74 (m, 2H, H_4), 4.24

(m, 2H, H_2), 3.88 (m, 2H, H_3).

^{13}C NMR (25 °C, THF- d_8): δ 178.2 (s, CO), 76.2 (d, $J_{Rh-C} = 14$ Hz, CH_{COD}),

74.3 (d, $J_{Rh-C} = 9$ Hz, CH_{COD}), 31.7 (s, CH_2_{COD}), 31.5 (s, CH_2_{COD}), (-45 °C):

103.7 (s, C_7H_7, C_1), 75.9 (s, C_7H_7, C_4), 68.4 (s, C_7H_7, C_2), 53.3

(s, C_7H_7, C_3).

4.5.3. Synthesis of *cis*-(μ - C_7H_7)Os(CO) $_3$ Rh(COD), 2b.

$Ph_4As[(C_7H_7)Os(CO)_3]$ (390 mg, 0.52 mmoles) was prepared in THF from KOtBu (58 mg, 0.52 mmoles) and (η^4 - C_7H_8)Os(CO) $_3$ (190 mg, 0.52 mmoles) followed by immediate reaction with a slurry of $AsPh_4Cl$ (0.22 g 0.52 mmoles), also in THF. After separating the dark red THF solution from the precipitated KCl, the anion was added to $[Rh(COD)Cl]_2$ (0.13 g, 0.26 mmoles) in THF at -78 °C. The resultant orange THF solution was allowed to warm to room temperature overnight with stirring under nitrogen. The solvent was then removed to give an orange-brown residue which was extracted with toluene (3 x 10 ml). The combined orange extracts were separated from the resultant oily brown residue,

concentrated to 2 ml and chromatographed on a silica gel column (2.2 x 7.5 cm) eluting with hexane. One red band was collected and the solution was concentrated to 5 ml and cooled to -78 °C to give bright red crystals of **2b** (65 mg, 22%). Concentration of the mother liquor to 1 ml yielded a further 25 mg (30% overall).

Anal. Calcd. for $C_{18}H_{19}O_3OsRh$: C, 37.50, H, 3.32. Found: C, 37.59, H, 3.31.

Mass Spectrum (70 eV, 110 °C): M^+ , $M^+ - nCO$ ($n = 1 - 3$).

IR (hexane): ν_{CO} 2030(s), 1962(s), 1957(s) cm^{-1} .

^1H NMR (25 °C, CD_2Cl_2): δ 3.68 (s, 11H, $C_7H_7 + CH_{COD}$), 2.50 (s, 4H, CH_2_{COD}), 2.30 (s, 4H, CH_2_{COD}), (-90 °C): 4.50 (m, 2H, H_4), 4.10 (m, 1H, H_1), 3.56 (m, 4H, $H_2 + CH_{COD}$), 3.48 (m, 2H, CH_{COD}), 2.54 (m, 4H, $H_3 + CH_2_{COD}$), 2.22 (m, 6H, CH_2_{COD}).

^{13}C NMR (25 °C, CD_2Cl_2): δ 179.0 (s, CO), 80.8 (d, $J_{Rh-C} = 8Hz$, CH_{COD}), 58.1 (s, C_7H_7), 32.6 (s, CH_2_{COD}), (-93 °C): 182.0 (s, 2CO), 171.9 (s, CO), 79.8 (d, $J_{Rh-C} = 6Hz$, CH_{COD}), 78.7 (d, $J_{Rh-C} = 8Hz$, CH_{COD}), 77.3 (s, C_7H_7, C_4), 62.8 (s, C_7H_7, C_1), 50.9/40.0 (s/s, $C_7H_7, C_2/C_3$), 32.4 (s, CH_2_{COD}), 30.7 (s, CH_2_{COD}).

Note: The reaction of $K[(C_7H_7)Os(CO)_3]$ with $[Rh(COD)Cl]_2$ in THF also lead to a small amount (5%) of **2b** (see results section).

4.5.4. Isomerization of **2a** to **2b**.

To *trans*-($\mu-\eta^4, \eta^3-C_7H_7$) $Os(CO)_3Rh(COD)$ (**2a**) (20 mg, 0.035 mmoles) in THF (10 ml), was added PPNCI (9.4 mg, 0.5 equivalent) at room temperature under nitrogen. Over fifteen minutes the solution slowly

darkened from a light yellow to a pale orange-brown colour. The solvent was removed to give a yellow-brown residue which was extracted with toluene and chromatographed on a silica gel column (1.1 cm x 8 cm) and eluted with hexane to give one strong yellow band which was collected. The solvent was then removed and the orange compound was crystallised from a minimum volume of hexane to give bright red crystals of **2b** (5 mg, 25%).

4.5.5. Preparation of *cis*-(μ -C₇H₇)Os(CO)₃Rh(CO)₂, **2c**

Cis-(μ - η^3, η^4 -C₇H₇)Os(CO)₃Rh(COD) (**2b**) (11 mg, 0.019 mmoles) was dissolved in hexane (8 ml) in a 50 ml round bottom flask fitted with a side arm. The yellow solution was freeze-thaw degassed twice and then an atmosphere of carbon monoxide (50 ml at room temperature and pressure, ca 2.23 mmoles) was introduced to the flask. The solution was stirred for 2.5 hours during which time the solution changed from yellow to orange. The solvent was then removed and the residue was crystallised from hexane (ca. 0.5 ml) to give **2c** as a rust-orange solid (4 mg, 40%).
Anal. Calcd. for C₁₂H₇O₅OsRh: C, 27.49, H, 1.35. Found: C, 27.61, H, 1.26.

Mass Spectrum (70 eV, 180 °C): M⁺, M⁺-*n*CO (*n* = 1 - 5).

IR (hexane): ν_{CO} 2063(s), 2032(s), 2019(s), 1980(m) cm⁻¹.

¹H NMR (25 °C, CD₂Cl₂): δ 4.08 (s, 7H, C₇H₇).

¹³C NMR (25 °C, CD₂Cl₂): δ 193.0 (d, J_{Rh-C}=70Hz, CO_{Rh}), 176.7 (s, CO_{Os}), 56.9 (s, C₇H₇).

4.5.6. Preparation of $(\mu\text{-C}_7\text{H}_7)(\mu\text{-dppm})\text{Os}(\text{CO})_2\text{Rh}(\text{CO})$, **2d**.

A solution of *trans*- $(\mu\text{-}\eta^4, \eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{Rh}(\text{COD})$ (**2a**) (16 mg, 0.028 mmoles) in degassed benzene (5 ml) was slowly added to DPPM (11 mg, 0.028 mmoles) also in degassed benzene (5 ml). The solution, which turned to a red-orange colour upon addition was then allowed to stir for 10 minutes at room temperature with no further colour change. The solvent was then removed to leave a dark red residue which was crystallised from toluene/hexane at -40°C to give dark red crystals of $(\mu\text{-C}_7\text{H}_7)(\mu\text{-dppm})\text{Os}(\text{CO})_2\text{Rh}(\text{CO})$ (**2d**) (20 mg, 80%).

Anal. Calcd. for $\text{C}_{35}\text{H}_{29}\text{O}_3\text{P}_2\text{OsRh}$: C, 49.30, H, 3.43. Found: C, 50.12, H, 3.65.

IR (CH_2Cl_2) ν_{CO} : 1974(s), 1937(s), 1894(m) cm^{-1} .

^1H NMR (0°C , C_6D_6): δ 7.70 (t, $J_{\text{H-H}}=8\text{Hz}$, 2H, Ph), 7.58 (t, $J_{\text{H-H}}=8\text{Hz}$, 2H, Ph), 7.41 (t, $J_{\text{H-H}}=8\text{Hz}$, 2H, Ph), 7.33 (t, $J_{\text{H-H}}=8\text{Hz}$, 2H, Ph), 7.02 (m, 3H, Ph), 6.89 (m, 6H, Ph), 6.75 (m, 3H, Ph), 3.87 (m, 1H, CH_2), 3.55 (s, 7H, C_7H_7), 1.91 (m, 1H, CH_2).

^{31}P NMR (25°C , C_6D_6): δ 63.5 (dd, $J_{\text{P-P}}=123\text{Hz}$, $J_{\text{P-Rh}}=161\text{Hz}$), 19.9, (d, $J_{\text{P-P}}=123\text{Hz}$).

^{13}C NMR (25°C , C_6D_6): δ 199.0 (dd, $J_{\text{P-C}}=13\text{Hz}$, $J_{\text{Rh-C}}=75\text{Hz}$, CO_{Rh}), 137.3-128.4 (Ph), 55.9 (s, C_7H_7), 43.7 (t, $J_{\text{P-C}}=35\text{Hz}$, CH_2).

4.5.7. Synthesis of *cis*- $(\mu\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{Ir}(\text{COD})$, **3b**.

The reaction of $\text{Ph}_4\text{As}[(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3]$ (0.140 g, 0.165 mmoles) with $[\text{Ir}(\text{COD})\text{Cl}]_2$ (0.055 g, 0.082 mmoles) was carried out in a similar fashion to the preparation of **2b**. The resultant yellow-orange THF solution at -78°C

$^{\circ}\text{C}$ was stirred for 1.5 hours and warmed slowly to -10°C to give a dark yellow-brown solution. Further warming to $+10^{\circ}\text{C}$ gave reformation of the original yellow orange coloration after which no further colour changes were observed. The solvent was removed at room temperature to give an orange-brown residue which was extracted with toluene to give a yellow solution. Chromatography on a silica gel column (2.2 x 7.5 cm) with elution by hexane developed a yellow-green band which was collected. The solvent was removed and the yellow solid was crystallised from hexane at -78°C to give yellow crystals which proved to be *cis*-(μ - C_7H_7)Os(CO) $_3$ Ir(COD), **3b** (16 mg, 15%). Attempts to isolate the kinetic trans product proved unsuccessful.

Mass Spectrum (70 eV, 150°C): M^+ , $\text{M}^+ - n\text{CO}$ ($n = 1 - 3$).

IR (hexane): ν_{CO} 2038(s), 1972(s), 1962(s) cm^{-1} .

^1H NMR (25 $^{\circ}\text{C}$, toluene- d_8): δ 4.00 (br, C_7H_7), 3.64 (m, 2H, CH_{COD}), 3.35 (br, C_7H_7), 2.87 (m, 2H, CH_{COD}), 2.74 (m, 2H, CH_2COD), 2.33 (m, 2H, CH_2COD), 2.12 (m, 2H, CH_2COD), 1.96 (m, 2H, CH_2COD), (-30°C): 3.81 (m, 2H, $\text{C}_7\text{H}_7, \text{H}_4$), 3.30 (t, $J=6\text{Hz}$, 2H, $\text{C}_7\text{H}_7 \text{H}_2$), 3.07 (t, $J=6\text{Hz}$, $\text{C}_7\text{H}_7, 1\text{H}, \text{H}_1$), 2.03 (m, 2H, $\text{C}_7\text{H}_7, \text{H}_3 + 2\text{H}, \text{CH}_2\text{COD}$), ($+80^{\circ}\text{C}$): 3.34 (s, 7H, C_7H_7).

^{13}C NMR (0 $^{\circ}\text{C}$, toluene- d_8): δ 180.2 (s, CO_e), 165.6 (s, CO_a), 75.9 (s, C_4), 69.2 (s, C_1), 63.9, 62.9 (s, CH_{COD}), 41.7 (s, C_2), 38.6 (s, C_3), 34.6, 33.6 (s, CH_2COD).

4.5.8. X-ray Structure Determination of **2a**.

X-ray quality crystals of **2a** were obtained from CH_2Cl_2 /hexane over 2 days at -40°C . The structure was solved by Dr. B. D. Santarsiero of the

Structure Determination Laboratory of this department. The following information was obtained from the structure report (File number SDL:TAK8901). A suitable crystal was mounted on a glass fiber with epoxy, and optically centred in the x-ray beam of an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using MoK α radiation ($\lambda = 0.71073$ Å) with a graphite crystal, incident beam monochromator. The automatic peak search and reflection indexing programs generated a triclinic preliminary unit cell, and the cell volume indicated two molecules in the unit cell. Of the two possible space groups, P1 or P1, the centrosymmetric space group was chosen, with one molecule in the asymmetric unit. This was confirmed by satisfactory solution of the structure. The intensity data were collected at room temperature (23 °C) using a $\theta - 2\theta$ scan of fixed speed, 2.0 °/min. Backgrounds for the peaks were measured by extending the scan 25% on each side; this gave a peak to background counting time ratio of 2:1. The positions of the Os and Rh atoms were derived from a Patterson map, and R began at 0.19. The structure was refined, all hydrogen atoms isotropic, and all other atoms anisotropic, by using full matrix least squares techniques³¹. An empirical absorption correction was applied, using the Fourier filter scheme of Walker and Stuart³². The highest peak in the final difference Fourier has a density of 2.1 e/Å³. A summary of the crystallographic data is presented in Table 4.8. Positional and equivalent isotropic parameters for the non-hydrogen atoms are given in Table 4.9.

4.5.9. X-ray Structure Determination of **2b**.

X-ray quality crystals of **2b** were grown by slow evaporation of a benzene solution of **2b** in air. The structure was solved by Dr. B. D. Santarsiero of the Structure Determination Laboratory of this department. The following information was obtained from the structure report (File number SDL:TAK8903). A bright orange crystal of **2b** with the dimensions of 0.097 x 0.188 x 0.342 mm was selected and mounted on a glass fiber with epoxy, and optically centred in the x-ray beam of an Enraf-Nonius CAD4 automated diffractometer. The crystal was cooled to -20 °C with a cooled and dried air stream, and all measurements were made at this temperature. The automatic peak search and reflection indexing programs generated an orthorhombic cell. The systematic absences of $0kl, k + l$ odd and $h0l, h + l$ odd and the magnitude of the unit cell volume ($Z = 4$) led to the choices of space group as $Pnn2$ or $Pnnm$ (molecule with internal mirror plane). The centrosymmetric space group $Pnnm$ was initially chosen and was confirmed by satisfactory solution of the structure. The data were collected in similar fashion to **2b**. The positions of the Os and Rh atoms were derived from a Patterson map, and R began at 0.25. The structure was refined, all hydrogen atoms isotropic, and all other atoms anisotropic, by using full matrix least squares techniques³¹. An empirical absorption correction was applied, using the Fourier filter scheme of Walker and Stuart³². The highest peak in the final difference Fourier has a density of 1.3(2) e/Å³. A summary of the crystallographic data is presented in Table 4.8. Positional and equivalent isotropic parameters for the non-hydrogen atoms are given in Table 4.10.

Table 4.8. Summary of Crystallographic Data for **2a** and **2b**.

	2a	2b
empirical formula	C ₁₈ H ₁₉ O ₃ OsRh	C ₁₈ H ₁₉ O ₃ OsRh
crystal dimensions (mm)	0.071 x 0.136 x 0.202	0.097 x 0.188 x 0.342
space group	P1	Pnnm
a (Å)	6.718(3)	12.551(11)
b (Å)	11.378(4)	12.262(3)
c (Å)	11.527(4)	10.762(3)
α (deg)	81.813(23)	
β (deg)	79.215(29)	
γ (deg)	78.233(24)	
Z (Molecules/cell)	2	4
V (Å ³)	842.3	1656
d (calcd), (g/cm ³)	2.273	2.312
linear abs coeff μ , (cm ⁻¹)	85.23	86.68
mol wt	576.46	576.46
detector to sample dist (cm)	20.5	20.5
scan type	θ - 2 θ	θ - 2 θ
scan speed (deg/min)	2.0	2.0
scan width (deg)	1.20 + 0.35tan(θ)	0.80 + 0.35tan(θ)
aperture size (mm)	2.40 x 4.0	2.40 x 4.0
2 θ limit (deg)	56	50
data collection index range:	$\pm h, k, \pm l$	h, k, l
total no. of reflctns	4044 total, averaged; * 3202 with $I > \sigma(I)$	1636 total, averaged; 1265 with $I > 2\sigma(I)$
observations:variables ratio:	3202:208	1265:112
Agreement factors, R1, R2, GOF:	0.064, 0.058, 1.60	0.034, 0.040, 1.55

Table 4.9. Positional and equivalent isotropic parameters for the non-hydrogen atoms in 2a.

Atom	x	y	z	U_{eq}
Os	2037.5(7)	3918.3(4)	2388.9(5)	39.4(1)
Rh	3303.6(12)	61.5(7)	2699.1(7)	23.8(2)
C1	5261(15)	1168(9)	3115(9)	33(3)
C2	3407(17)	1360(9)	3907(9)	37(3)
C3	1542(17)	2290(9)	3692(11)	43(4)
C4	412(17)	2396(10)	2707(13)	59(5)
C5	1465(20)	2450(11)	1546(12)	66(4)
C6	3665(19)	2391(10)	1349(9)	44(4)
C7	5217(18)	1425(9)	1890(10)	41(4)
C8	4343(18)	4205(10)	2955(12)	49(4)
O8	5745(14)	4255(10)	3346(11)	87(4)
C9	5(18)	4966(10)	3330(13)	56(4)
O9	-1173(16)	5595(9)	3914(11)	82(4)
C10	2114(23)	5049(12)	1043(12)	68(5)
O10	2125(22)	5747(11)	207(11)	111(5)
C11	2948(18)	-723(10)	1179(10)	43(4)
C12	4640(18)	-1384(10)	1638(9)	39(3)
C13	4698(20)	-2592(10)	2326(11)	49(4)
C14	4094(20)	-2529(10)	3659(10)	46(4)
C15	2649(17)	-1399(10)	4010(9)	37(3)
C16	882(16)	-910(9)	3554(9)	33(3)
C17	90(17)	-1517(12)	2673(10)	49(4)
C18	839(17)	-1051(11)	1373(10)	52(4)

$U_{eq} = \frac{1}{3} \sum_{i=1}^3 r_i^2$, where r_i are the root-mean-square amplitudes of the AGDP.

Atom Coordinates ($\times 10^4$) and U_{eq} 's ($\times 10^3$)

Table 4.10. Positional and equivalent isotropic parameters for the non-hydrogen atoms in 2b.

Atom	x	y	z	$U_{eq}, \text{\AA}^2$
Os	2897.0(3)	465.1(3)	0	22.0(1)
Rh	2048.1(6)	2659.6(6)	0	20.0(2)
O8	3472(8)	-1930(7)	0	63.48
O9	4444(5)	1099(5)	2042(7)	61.17
C8	3249(9)	-1023(9)	0	32.61
C9	3870(6)	868(7)	1252(8)	37.04
C1	1212(9)	-53(10)	0	42.62
C2	1372(6)	528(5)	1145(7)	29.87
C3	1131(6)	1683(6)	1347(7)	29.43
C4	431(5)	2359(5)	651(7)	29.41
C10	4234(7)	3652(8)	693(9)	61.17
C11	3182(6)	3345(6)	1327(7)	34.74
C12	2276(6)	3999(6)	1311(7)	34.05
C13	2215(10)	5081(8)	654(10)	84.14

The equivalent isotropic Gaussian parameter U_{eq} is $\frac{1}{3} \sum_{i=1}^3 r_i^2$, where r_i are the root-mean-square amplitudes of the AGDP.

Positional ($\times 10^4$) and Gaussian ($\times 10^3$) Parameters

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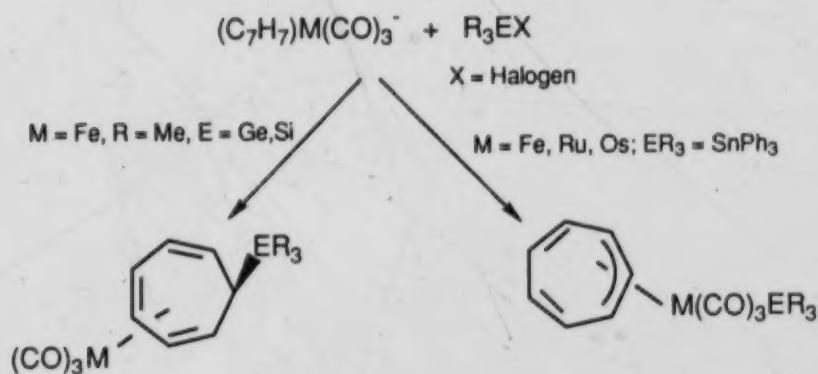
Chapter 5.

Solid-State Structure and Fluxional Solution Behaviour of the Ambident Organometallic Nucleophiles $(C_7H_7)M(CO)_3^-$ ($M = Fe, Ru, Os$)¹.

5.1. Introduction.

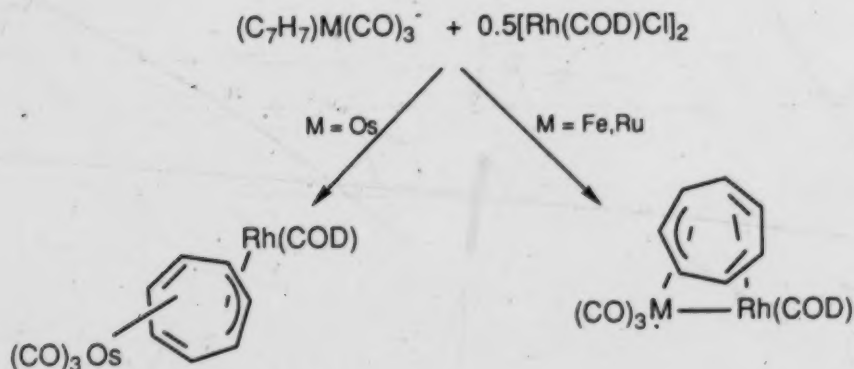
Anionic complexes of the transition metals are well known for their ability to produce metal-carbon and metal-metal bonds upon reaction with suitable electrophilic substrates². In earlier chapters, the synthesis and ambident nature of the anionic complexes, $(C_7H_7)M(CO)_3^-$ [$M = Fe$ (**1a**), Ru (**1b**), Os (**1c**)] have been discussed. The metal-dependent reactivity of these complexes with electrophiles is shown in Schemes 5.1 and 5.2. Thus, the reaction with R_3SiCl and R_3GeBr gives ring substituted complexes³, whereas Ph_3SnCl results in fluxional $\eta^3-C_7H_7$ complexes containing a $M-Sn$ bond⁴, Scheme 5.1.

Scheme 5.1



In accord with the reaction of Ph_3SnCl , transition metal based electrophiles were found to react with **1a** and **1b** to give cycloheptatrienyl bridged heterobimetallic complexes^{4b,5} where the two metals occupy the same face of the ring. However, as shown in Chapter 4, the reaction of **1c** ($\text{M} = \text{Os}$) with $[\text{Rh}(\text{COD})\text{Cl}]_2$ gives the isomeric unsaturated complex where Os and Rh are bonded to opposite faces of the C_7H_7 ligand⁶, Scheme 5.2.

Scheme 5.2



A possible reason for the variable reactivity exhibited by complexes **1** could be the availability, on the basis of the effective atomic number rule, of two bonding alternatives between the ring and the metal carbonyl fragment. These are shown on the next page. Changes in the predominant structural form in solution with the transition metal or differential sampling of the two forms by the electrophilic reagents could be the reason for the observed reactivity. Alternatively, it is also possible that changes in the interactions between the organic and inorganic

partners, in either form, as the metal is varied and the attendant changes in charge distribution, could be the sole reason for the electrophilic discrimination displayed by complexes **1**.



Clearly, in order to rationalize the observed reactivities, a precise knowledge of the bonding between the seven membered ring and the metal tricarbonyl fragment is necessary, both in the solid state and in solution. The solid state structure of **1a** has been determined and shown to conform to form A⁷. The ground state structural preference for the η^3 -bonded cycloheptatrienyl ring was also demonstrated by extended Huckel MO calculations⁸. Surprisingly for the Fe complex, **1a** it was found that there is more charge localization on the ring in this structure than in the η^4 -bonding alternative (B) which features a 'free' allyl anion fragment. However the calculations also showed that the η^4 -bonded structure (B) is only slightly less stable (14.2 kJ mol^{-1}) than bonding form A. The small energy difference between the two structures was used to rationalize the fluxional nature of **1a** in solution at room temperature and below. In this chapter, the solid state structures of compounds **1b** and **1c** and the results of variable temperature NMR studies with a view to establish the solution structure of these anionic species are reported.

5.2. Results.

5.2.1. Solid State Structure of $(C_7H_7)M(CO)_3^-$ compounds.

X-ray quality crystals of $[Ph_4As][(C_7H_7)M(CO)_3]$ [$M = Ru$ (**1b**), and Os (**1c**)] were obtained from THF/toluene solutions of the respective anions. The structure determinations were carried out by J. C. Huffman and W. E. Streib of the Molecular Structure centre, Department of Chemistry, University of Indiana. In the solid state, complexes **1b** and **1c** were found to be isomorphous, and nearly isostructural. The unit cell contains well separated Ph_4As^+ cations and $(C_7H_7)M(CO)_3^-$ anions. There are only subtle differences in the structure of the $(C_7H_7)M(CO)_3^-$ moiety in **1b** and **1c**. Two perspective views of the anionic organometallic constituent (of **1b** and **1c**) are shown in Figure 5.1 which also establishes the numbering system. Important bond distances and angles, together with those of **1a** for comparison, are listed in Tables 5.1 and 5.2. It is clear from the figure that the cycloheptatrienyl ring is bonded to the metals in an η^3 -fashion in both complexes. This type of structure has already been seen for the analogous iron compound **1a** and its stability over the alternative η^4 -bonded cycloheptatrienyl form (see A and B) has also been predicted on the basis of extended Huckel molecular orbital calculations. The similarities in bonding between **1a** - **1c** are vividly apparent from Tables 5.1 and 5.2. Differences in bond lengths can mostly be accommodated by differences in metallic radii⁹.

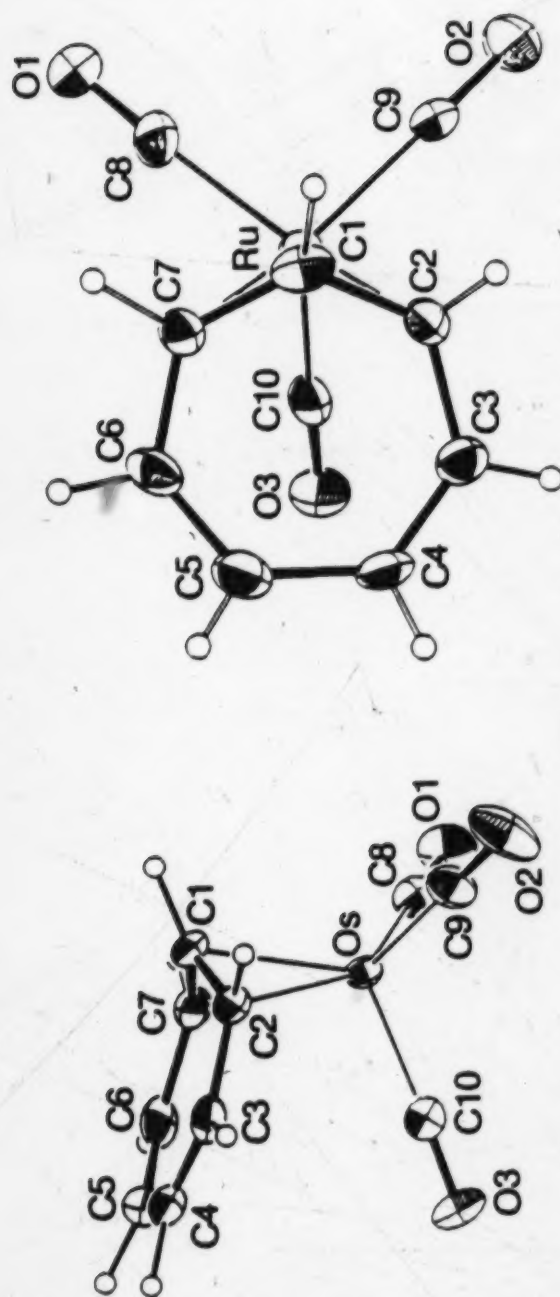


Figure 5.1. Perspective views of $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3^-$ [**1b** ($\text{M} = \text{Ru}$), **1c** ($\text{M} = \text{Os}$)].

Table 5.1. Selected Bond Lengths for Anions **1**, (η^3 -C₇H₇)M(CO)₃ (M = Fe, Ru, Os)^a.

Bond length	Fe ^b (1a)	Ru (1b)	Os (1c)
met. rad ^c	1.16	1.25	1.26
M - C1	1.983(10)	2.113(7)	2.124(5)
M - C2	2.113(12)	2.230(7)	2.244(5)
M - C7	2.137(11)	2.252(7)	2.244(5)
M - C8	1.780(13)	1.901(7)	1.900(6)
M - C9	1.755(13)	1.904(7)	1.898(6)
M - C10	1.765(12)	1.941(7)	1.922(5)
C1 - C2	1.432(21)	1.432(10)	1.448(8)
C2 - C3	1.429(22)	1.468(10)	1.459(8)
C3 - C4	1.305(25)	1.350(11)	1.348(8)
C4 - C5	1.428(24)	1.429(12)	1.438(9)
C5 - C6	1.344(23)	1.358(11)	1.342(9)
C6 - C7	1.421(24)	1.462(10)	1.455(8)
C7 - C1	1.412(22)	1.425(11)	1.439(8)
C8 - O1	1.130(15)	1.161(8)	1.154(6)
C9 - O2	1.163(15)	1.142(9)	1.155(7)
C10 - O3	1.138(14)	1.139(8)	1.146(6)

a. Standard deviations are given in parentheses. b. From reference 7. c. From reference 9.

Table 5.2. Selected Bond Angles for Anions 1, $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3$ (M = Fe, Ru, Os)^a.

Bond Angles	Fe ^b (1a)	Ru (1b)	Os (1c)
C2 - M - C1	41.3	38.4(3)	38.6(2)
C3 - M - C2	69.8	66.8(3)	66.7(2)
C7 - M - C1	39.7	37.9(3)	38.3(2)
C8 - M - C9	97.6	94.9(3)	94.6(2)
C9 - M - C10	104.8	108.6(3)	108.0(2)
C10 - M - C8	106.6	106.8(3)	106.7(2)
C1 - C2 - C3	127.9	125.4(7)	126.2(5)
C2 - C3 - C4	131.7	130.8(7)	130.3(6)
C3 - C4 - C5	125.9	126.9(7)	127.3(6)
C4 - C5 - C6	127.9	128.4(7)	127.6(6)
C5 - C6 - C7	130.3	129.0(7)	130.5(6)
C6 - C7 - C1	128.8	127.4(7)	126.3(5)
C7 - C1 - C2	117.1	119.4(6)	117.5(5)
M - C8 - O1	175.8	176.2(6)	177.3(5)
M - C9 - O2	177.4	177.8(6)	178.7(5)
M - C10 - O3	179.1	175.8(6)	176.9(5)

a. Standard deviations are given in parentheses. b. From reference 7.

The length of the C-O bond of the carbonyl ligands are almost identical. In the case of the Ru and Os complexes the CO ligand underneath the C₇H₇ ring has the marginally longer M-C bond, in accord with its apical position in what can be described as quasi square pyramidal geometry of the central metal atoms. The allylic C-C bond lengths, at about 1.43 Å, are normal and very similar in all three cases. The other C-C bond distances are alternatively long and short. As expected the metal-carbon bond distance to the central allylic carbon atom is shorter than the distances to the terminal positions¹⁰, in all three cases. The distances in the Ru and Os complexes are very similar. The ligand is hinged at the terminal allylic carbons into two planes with the interplanar angle being 37.2° for Os and 35.7° for Ru. The same angle for Fe is 31.3° which implies a decrease in conjugation between the allylic and butadiene fragments as one proceeds from Fe to Ru to Os. In unison with this, the two parts of the ligand (allyl and diene) are separated by longer bonds for Ru and Os (typically 1.46 Å) than for Fe (1.42 Å).

5.2.2. Fluxional Solution Behaviour of Compounds 1.

The variable temperature ¹H NMR spectrum of the Os complex **1c**, is shown in Figure 5.2. As can be seen, the single sharp line at room temperature broadens upon lowering the temperature and disappears into the baseline at -65 °C. The low temperature limiting spectrum is reached at -110 °C, and at this stage the spectrum consists of four signals in the intensity ratio 2:2:2:1. The absolute assignment of the resonances was determined from H-H couplings obtained from resolution enhancement of

Figure 5.2.

Variable Temperature ^1H NMR Spectra of $[\text{AsPh}_4][(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3]$

* = THF, ‡ = residual toluene.



the spectrum of **1c** at $-115\text{ }^{\circ}\text{C}$. The peak of intensity 1 is clearly the central allylic hydrogen (H1) and is split into a triplet by the neighbouring protons, the H2 signal with a coupling constant of 4.5 Hz. H2 is a doublet of doublets with coupling constants of 4.5 and 7.5 Hz to H1 and H3 respectively. As expected, H3 is a complex multiplet, whilst H4 has a doublet of doublets appearance with coupling constants of 8.3 (^3J) and 3.7 Hz (^4J) to H3. The chemical shifts of the signals are clearly indicative of an η^3 bonding mode by comparison with the slow limiting NMR spectra of other known trihapto cycloheptatrienyl complexes¹¹. As in **1c**, in the ^1H NMR spectra of these complexes the bound allylic hydrogens are typically at relatively high field, whilst the lowest field resonance is due to the outer diene positions (Table 5.3). In the alternative η^4 structure, one would expect the ^1H and ^{13}C resonances of the bound diene positions to be at much higher field.

In all cases studied so far, the mechanism of the fluxional process in η^3 -cycloheptatrienyl complexes involves a series of 1,2-metal shifts around the seven membered ring^{4a,11}. The operation of the same mechanism in **1c** is given support by the slower broadening of the H4 signal upon warming from $-115\text{ }^{\circ}\text{C}$. Simulation of the spectra at different temperatures yielded an activation energy, $\Delta G^\ddagger$, of 8.2 kcal mol^{-1} for this process in **1c**. It should be noted at this point that although the η^3 - and η^4 -bonding modes of the C_7H_7 ring are very close in energy and this has been used to account for the facile fluxionality of **1a**⁸, the 1,2-metal shift process does not require passage through the η^4 - C_7H_7 form¹¹. The slow limiting

Table 5.3.

^1H and ^{13}C NMR Data of the $\eta^3\text{-C}_7\text{H}_7$ Ligand in **1** and Related Complexes^a.

Compound	H1/C1	H2/C2	H3/C3	H4/C4	Temp (°C)	^1H Ave	Tc (°C)	^{13}C Ave
1 a						4.90	-150 ^b	95.2
1 b						4.58	-115	92.8
1 c	2.19	3.83	6.42	4.87	-115	4.66	-65	89.2
	38	38	142	112				
3^c	2.10	4.27	6.00	5.00	-140	5.63 ^d	-110 ^d	103.8 ^d
4^e	3.39	4.40	5.98	5.19	-94	5.00	-10	97.3
	61.7	51.9	133.9	119.3				

a Chemical Shifts (δ) in ppm from TMS in THF-*d*₈ (unless otherwise noted).

b Low temperature spectrum recorded as the PPN⁺ salt in a mixture of CHF₂Cl/CD₂Cl₂ (4:1)^{11c}.

c **3** is ($\eta^3\text{-C}_7\text{H}_7$)Co(CO)₃, spectrum in CF₂Cl₂^{11b}.

d Unpublished results, Hager, D.; Edelmann, F.; Takats, J.

e **4** is the symmetrical isomer of ($\eta^3\text{-C}_7\text{H}_7$)Os(CO)₃SnPh₃, spectrum in CD₂Cl₂^{4c}.

spectrum for the Ru analogue was not obtained as it would have required considerably lower temperature than for **1c**. The variable temperature ^1H NMR spectra of **1b** does however show considerable broadening of the cycloheptatrienyl ring signal with the coalescence temperature approached in THF at $-100\text{ }^\circ\text{C}$. The ^1H NMR spectrum of **1a** shows rapid ring whizzing of the cycloheptatrienyl ring at $-100\text{ }^\circ\text{C}$ although broadening of the single peak does occur below this temperature with the coalescence temperature reached at $-150\text{ }^\circ\text{C}$ ^{11c}. The low temperature ^{13}C NMR spectrum of **1c** is also recorded in Table 5.3. At $-100\text{ }^\circ\text{C}$, the ring signals are still not very sharp and the resonances for C1 and C2 overlap because of the proximity of their chemical shifts.

5.3. Discussion

The solid state structure of all three complexes conform to the $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3$ bonding form A. In solution **1c** was also shown to exhibit this bonding fashion indicating that complexes **1a** and **1b** are most likely to adopt this ligand bonding in solution as well. Thus the reactivity difference and electrophilic discrimination of compounds **1**, may not be related to the facility of the η^3 to η^4 interconversion, or the energy difference between the two forms, but to the variation in the metal to $\eta^3\text{-C}_7\text{H}_7$ ligand binding as the transition metal is changed.

In order to easily visualize the relevant bonding interaction the molecular orbitals of $\text{Fe}(\text{CO})_3$ and C_7H_7 fragments adapted from reference 8

together with the well known molecular orbitals of the related allyl fragment are shown in Figure 5.3. A clear difference between the allyl and $\eta^3\text{-C}_7\text{H}_7$ moieties is immediately apparent. For the allyl group, the $1\pi_a$ molecular orbital has the best energy match for interaction with the metal frontier orbitals. This ligand orbital has a node at the central allyl carbon atom. The situation with the $\eta^3\text{-C}_7\text{H}_7$ ligand is different. Although the degeneracy of the molecular orbital pairs of C_7H_7 under D_{7h} symmetry is lifted in compounds **1**, the energy difference between the two 3π molecular orbitals is not expected to be large and consequently both may still be responsible for the main interaction with the $\text{M}(\text{CO})_3$ fragment. Note that the 3π MO has significant amplitude at the central carbon of the $\eta^3\text{-C}_7\text{H}_7$ moiety. In accord with these considerations, the ^1H and ^{13}C signals of the central allyl atom resonate at the low field positions¹² (See Table 5.4). Substantial upfield shift in the position of these signals is seen only in dinuclear complexes containing bridging C_3H_5 moieties, where strong $\text{Md}\pi$ to $2\pi_s$ bonding is possible. A particularly striking example is the dinuclear Ni complex, $(\text{P}^i\text{Pr}_3)_2\text{Ni}_2(\mu\text{-Cl})(\mu\text{-C}_3\text{H}_5)$ ¹³ (**9**). On the other hand, in compounds containing the $\eta^3\text{-C}_7\text{H}_7$ unit, the central ^1H and ^{13}C signals are at high field, because the HOMO's from the metal ($2e_s$, $2e_a$) and C_7H_7 ($3\pi_s$, $3\pi_a$) have substantial localization at the central atom (see Table 5.4). Consistent with this postulate, although perhaps somewhat surprisingly, calculations have shown that in **1a** more charge is localised on the ring in the η^3 mode (bonding form A) than in form B which features a "free" allyl anion⁸.

Figure 5.3. Schematic Diagrams of the molecular orbitals of $\text{Fe}(\text{CO})_3$ with C_7H_7^- (D_{7h} symmetry), adapted from reference 8, and C_3H_5^- .

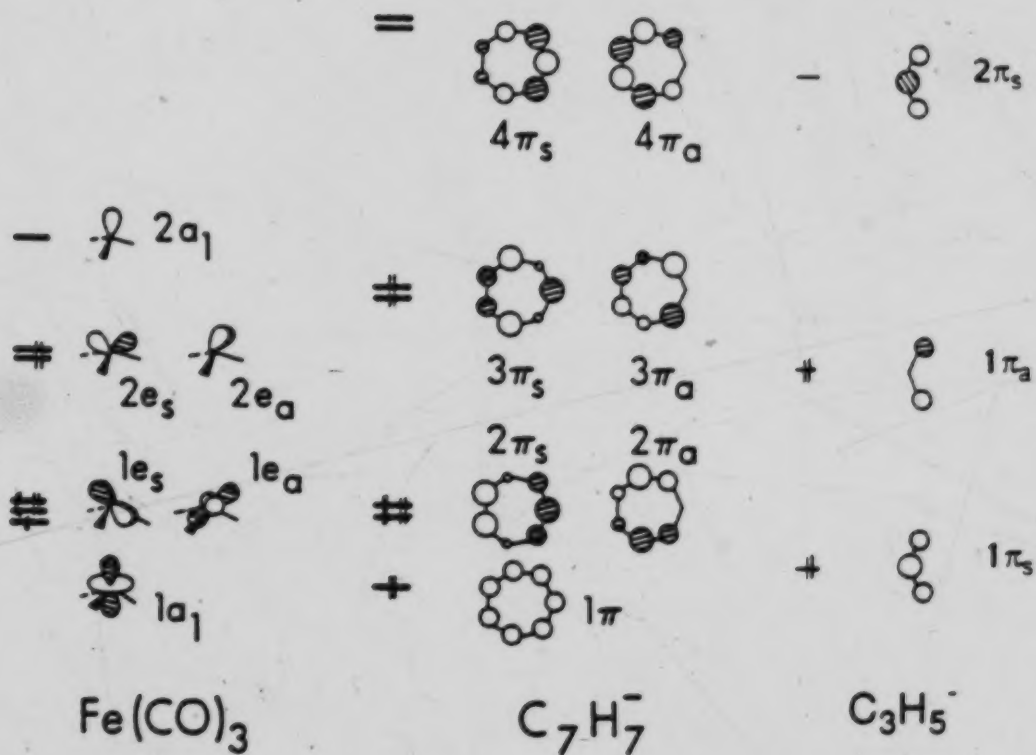


Table 5.4. ^{13}C NMR Data of Allylic Fragments Including $\eta^3\text{-C}_7\text{H}_7^{\text{a}}$.

Compound ^b	C1	C2	Reference
1 c	38	38	this work
4	61.7	51.9	4c
5	144.0	52.8	14b
6	94.5	29.1	c
7	119.0	57.6	17
8	83.9	30.7	18
9	34.8	21.9	15

a Chemical shifts (δ) in ppm, spectrum in THF- d_8 (unless noted below).

b **4** is the symmetrical isomer of $(\eta^3\text{-C}_7\text{H}_7)\text{Os}(\text{CO})_3\text{SnPh}_3$, spectrum in CD_2Cl_2 ; **5** is KC_3H_5 ; **6** is $(\eta^3\text{-C}_3\text{H}_5)\text{Os}(\text{CO})_3\text{H}$, spectrum in CD_2Cl_2 ; **7** is $\text{K}(\text{C}_9\text{H}_9)$ (BCNT); spectrum in DME- d_{10} ; **8** is $(\text{BCNT})_2\text{Fe}$, spectrum in C_6D_6 ; **9** is $(\text{P}^i\text{Pr}_3)_2\text{Ni}_2(\mu\text{-Cl})(\mu\text{-C}_3\text{H}_5)$, spectrum in toluene d_8 .

c Unpublished results, Kiel, G.-Y.; Takats, J.

It is worth noting that the ^{13}C chemical shifts of carbanions have been related to Π electron density¹⁴. For instance, in KC_3H_5 (5) the calculated Π electron densities of the terminal allylic carbons is 1.51 whereas that of the central carbon is 0.97 electrons¹⁴, with the larger density on the terminal carbons causing their upfield shift. The separation between the chemical shifts of the central and end carbons is 91 ppm (see Table 5.4). Although it is dangerous to make predictions concerning electron density on bound carbanionic ligands on the basis of their chemical shifts, because of the well known metal effect on ^{13}C chemical shifts^{12a}, it is clear that the C_7H_7 ligand in **1c** carries a large amount of negative charge. As would be expected from such considerations, the chemical shifts of anionic **1c** are at higher field than in the neutral **4**. The identical chemical shifts of C1 and C2 in **1c** is also remarkable and corroborates our suggestion of important back bonding to the central carbon as well.

Included in Table 5.4 is the organic anion BCNT^- (**7**)¹⁵ and its iron complex $\text{Fe}(\text{BCNT})_2$ ¹⁶ (**8**). This anion contains an allylic fragment within a seven-membered ring, and whilst it is possible that there is some interaction involving the three unsaturated bridges¹⁵, the allylic portion is clearly more isolated than in cycloheptatrienyl complexes. This is reflected in the ^{13}C signals which resemble more closely the allyl anion.



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Although the low temperature limiting spectra has not been attained for **1a** and **1b**, the averaged ^{13}C chemical shift of the ring carbons (**1a**; 95.2, **1b**; 92.8, **1c**; 89.0 ppm, all in $\text{THF-}d_8$) show a trend consistent with increased negative charge on the cycloheptatrienyl ligand in the order $\text{Fe} < \text{Ru} < \text{Os}$. These chemical shifts can be compared to the neutral complexes $(\eta^3\text{-C}_7\text{H}_7)\text{M}(\text{CO})_2(\text{diphosphine})\text{I}$ ($\text{M} = \text{Mo}$; 105.3, $\text{M} = \text{W}$; 101.3)¹⁷. These observations can best be explained by an increased metal π basicity (toward the seven membered ring) upon descending the metal triad. A second consequence of such an increase in backbonding is the concomitant change to increased sp^3 character of the carbon atoms of the η^3 -allylic unit. This effect is therefore also helpful in explaining the decreased conjugation between the bound allylic and unbound diene fragments of the C_7H_7 ring for Ru and Os, and hence also the decreasing fluxional behaviour which is observed upon descending the metal triad. These observations are also in accord with the apparent increase in basicity of the anionic complexes going from Fe to Ru to Os. Indeed whilst deprotonation of $(\text{C}_7\text{H}_8)\text{M}(\text{CO})_3$ with KO^tBu occurs readily in THF ($\text{M} = \text{Fe}$, Ru, Os) at room temperature, upon cooling the solution to -78°C the reverse reprotonation reaction occurs only for the Os anion. Of course, this rationale is also useful in explaining other well known trends in organotransition metal chemistry such as increased metal-ligand bond strengths¹⁸, and olefin rotation barriers¹⁹ down a triad, and the preference for classical over non-classical hydrides²⁰ by electron rich metals.

5.4. Summary.

All three anionic complexes **1** contain an η^3 bonded cycloheptatrienyl ring as the ground state structure in the solid state. A decrease in conjugation between the allylic portion of the ring and the free diene is observed for Ru and Os. For the Os complex, the same structure is adopted in solution as deduced from the slow limiting ^1H and ^{13}C NMR spectrum. The slow limiting spectra could not be obtained for the Fe and Ru anions due to the higher rate of metal migration around the C_7H_7 ligand. In the osmium anion, **1c**, probably as a result of more effective back-bonding onto the allyl part of the ring there is apparently more negative charge delocalised on the ring than in the Fe and Ru congeners. As a consequence, its reactivity toward electrophilic reagents is even more unpredictable than that of **1a** and **1b**.

5.5. Experimental Section.

5.5.1. General Techniques and Reagents, Chapter 5.

X-ray quality crystals of **1b** and **1c** were grown in a Vacuum Atmospheres Model M040-2 glove box under purified nitrogen. The Complete solid-state structure determinations on **1b** and **1c** were carried out by J. C. Huffman, and W. E. Streib of the Molecular Structure Centre, Indiana University, Bloomington, Indiana, U.S.A. A limited amount of pertinent experimental data is extracted from the respective structure reports and included in this thesis for the sake of completeness. Further information including listings of observed and calculated structure factor amplitudes of all reflections may be obtained from Dr. J. Takats of this department. General operating procedures and listings of programs have been given elsewhere²¹. The variable temperature NMR spectra were recorded on a Bruker AM 400 spectrometer. In both instances the samples were prepared under inert atmosphere. $K[(C_7H_7)Ru(CO)_3]$ was prepared according to the literature procedure^{4b}. $[AsPh_4][(C_7H_7)Os(CO)_3]$ was prepared as described in Chapter 2.

5.2.2. Synthesis of $[AsPh_4][(C_7H_7)Ru(CO)_3]$, **1b**.

A dark red solution of $K(C_7H_7)Ru(CO)_3$ (ca. 0.58 g, 1.85 mmoles) was transferred under nitrogen to a separate flask containing a slurry of $AsPh_4Cl$ (0.77 g, 1.85 mmoles) in THF (30 ml). The solution was filtered and the solvent was removed to leave a dark orange-red residue which

was crystallised from THF/hexane at $-40\text{ }^{\circ}\text{C}$ to give large, dark red crystals of $[\text{AsPh}_4][(\text{C}_7\text{H}_7)\text{Ru}(\text{CO})_3]\cdot\text{THF}$ (**1b**) (0.72 g, 61%).

Anal, Calcd for $\text{C}_{38}\text{H}_{35}\text{AsO}_4\text{Ru}$: C, 62.38, H 4.82. Found: C, 62.69, H, 4.32.

IR (THF) ν_{CO} : 1960(s), 1885(s), 1864(s) cm^{-1} .

^1H NMR (25 $^{\circ}\text{C}$, $\text{THF}-d_8$): δ 7.7 - 7.9 (20H, Ph), 4.58, (s, 7H, C_7H_7).

^{13}C NMR (25 $^{\circ}\text{C}$, CD_2Cl_2): δ 213.0 (s, CO), 135.1 (s, Ph, *p*) 133.1 (s, Ph), 131.6 (s, Ph), 92.7, (s, C_7H_7).

5.5.3. Crystallographic Studies.

a) $[\text{AsPh}_4][(\text{C}_7\text{H}_7)\text{Ru}(\text{CO})_3]\cdot 0.5\text{C}_7\text{H}_8$, **1b**.

X-ray quality crystals were obtained from THF/toluene over 1 week at $-40\text{ }^{\circ}\text{C}$. The structure was solved by J. C. Huffman of the Molecular Structure Centre, Department of Chemistry, Indiana University. The following information has been taken from the structure determination report (number 88807). A suitable crystal was located and transferred to the goniostat using standard inert atmosphere handling techniques and cooled to $-155\text{ }^{\circ}\text{C}$ for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with no symmetry or systematic absences, indicating one of the triclinic space groups. Subsequent solution and refinement of the structure confirmed the centrosymmetric choice, P1.

Data were collected in the usual manner using a continuous θ - 2θ scan with fixed backgrounds. Data were reduced to a unique set of intensities and associated sigmas in the usual manner. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The compound of interest co-crystallizes with 0.5 molecules of toluene per asymmetric unit, the toluene molecule being on a crystallographic centre of symmetry. The methyl group on the toluene molecule is therefore disordered. A difference map revealed all of the hydrogen atoms except for the disordered methyl group. All hydrogen atoms which had been located were refined isotropically and non-hydrogen atoms anisotropically in the final cycles. No absorption correction was performed. A final difference Fourier was featureless, with the largest peak being $0.45 \text{ e}/\text{\AA}^3$.

b) $[\text{AsPh}_4][(\text{C}_7\text{H}_7)\text{Os}(\text{CO})_3] \cdot 0.5\text{C}_7\text{H}_8$, 1c.

Crystals were grown from THF/toluene at room temperature over 2 days. The structure determination was carried out by W. E. Streib of the Molecular Structure Centre, Department of Chemistry, Indiana University. The following information has been taken from the structure determination report (number 88808). A suitable crystal was mounted using silicone grease in a nitrogen atmosphere glove bag and was transferred to a goniostat where it was cooled to -143°C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space revealed no symmetry or systematic absences. A triclinic unit cell was found which was very similar to that of **1b**, indicating that the present structure was probably isomorphous with the earlier one. There was no

need to solve the structure. The coordinates for the non-hydrogen atoms in **1b** were used as a starting point and they quickly refined to an $R(F) = 0.033$. In the final cycles of refinement, the hydrogen atoms which had been located (i.e. all, except those of the disordered methyl group of the toluene solvate) were refined with isotropic thermal parameters and the non-hydrogen atoms were refined with anisotropic thermal parameters. No absorption correction was applied. The final difference map was essentially featureless. There were heavy atom residuals of less than $2 \text{ e}/\text{\AA}^3$. All other residual peaks were less than $0.5 \text{ e}/\text{\AA}^3$. A summary of the crystallographic data for compounds **1b** and **1c** is presented in Table 5.5. Positional and equivalent isotropic parameters of the anion, $(\text{C}_7\text{H}_7)\text{M}(\text{CO})_3^-$, are given in Tables 5.6 and 5.7.

Table 5.5. Summary of Crystallographic Data for 1b and 1c.

	1 b	1 c
empirical formula	$\text{RuAsC}_{34}\text{H}_{27.0.5}\text{C}_7\text{H}_8$	$\text{OsAsC}_{34}\text{H}_{27.0.5}\text{C}_7\text{H}_8$
colour of crystal	red	red
crystal dimensions (mm)	0.25 x 0.25 x 0.25	0.1 x 0.2 x 0.3
space group	P1	P1
cell dimensions (-155 °C)		
a (Å)	12.308(4)	12.314(2)
b (Å)	12.017(5)	12.025(2)
c (Å)	11.326(4)	11.331(2)
α (°)	71.18(2)	71.12(1)
β (°)	80.93(2)	80.87(1)
γ (°)	90.15(2)	90.08(1)
Z (Molecules/cell)	2	2
V (Å ³)	1563.23	1564.85
d (calcd), (g/cm ³)	1.499	1.700
wavelength	0.71069	0.71069
mol wt	705.65	800.78
linear abs coeff (cm ⁻¹)	15.734	51.597
detector to sample dist (cm)	22.5	22.5
sample to source dist (cm)	23.5	23.5
av ω scan width at half height (deg)	0.25	0.25
scan speed (deg/min)	8.0	6.0
scan width (deg + dispersn)	1.8	1.8
individual bkgd (s)	4	6
aperture size (mm)	3.0 x 4.0	3.0 x 4.0
2 θ range (deg)	6 - 45	6 - 45
total no. of reflctns collected	4129	7420
no. of unique intensities	4081	4106
no. of F > 0.0	3928	4024
no. of F > 3.0 σ (F)	3686	3905
R for averaging	0.030	0.018
R(F)	0.0567	0.0268
R _w (F)	0.0575	0.0278
goodness of fit for the last cycle	1.645	1.060
max Δ/σ for the last cycle	0.35	0.52
data collection index range	h, $\pm$ k, $\pm$ l	h, $\pm$ k, $\pm$ l

Table 5.6.

Fractional Coordinates^a and Equivalent Isotropic Thermal Parameters for
(C₇H₇)Ru(CO)₃⁻ in **1b**.

Atom	x	y	z	U _{iso} ^b
Ru	638.4(4)	2710.7(5)	7794(1)	20
C1	343(6)	1898(7)	6466(7)	29
C2	-369(6)	2858(6)	6283(7)	25
C3	-1573(6)	2747(7)	6657(7)	30
C4	-2244(6)	1841(7)	7469(8)	30
C5	-1919(6)	749(7)	8261(8)	35
C6	-885(6)	396(6)	8389(8)	32
C7	169(6)	957(6)	7640(7)	28
C8	1869(6)	2123(6)	8582(7)	30
C9	1306(6)	4249(7)	6920(7)	33
C10	-529(6)	2803(6)	9121(7)	25
O1	2649(4)	1826(5)	9032(5)	42
O2	1738(5)	5158(5)	6409(7)	61
O3	-1260(4)	2852(5)	9854(5)	38

^a Fractional coordinates are $\times 10^4$. U_{iso} values are $\times 10^3$.

^b Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, Acta. Cryst., 1959, 12, 609.

Table 5.7.

Fractional Coordinates^a and Equivalent Isotropic Thermal Parameters for
(C₇H₇)Os(CO)₃⁺ in 1c.

Atom	x	y	z	U _{iso} ^b
Os	653.6(2)	2716.0(2)	7788.8(2)	16
C1	346(4)	1878(5)	6478(5)	25
C2	-384(4)	2840(5)	6297(5)	24
C3	-1580(5)	2736(5)	6665(6)	27
C4	-2247(5)	1828(5)	7473(5)	29
C5	-1924(5)	730(5)	8275(6)	32
C6	-897(5)	389(5)	8388(6)	30
C7	1310(5)	4254(5)	6925(6)	32
C8	1886(4)	2146(5)	8578(5)	27
C9	1310(5)	4254(5)	6925(6)	32
C10	-502(4)	2809(5)	9104(5)	24
O1	2655(3)	1843(4)	9036(4)	38
O2	1726(4)	5180(4)	6390(5)	54
O3	-1224(3)	2868(4)	9851(4)	34

^a Fractional coordinates are $\times 10^4$. U_{iso} values are $\times 10^3$.

^b Isotropic values for those atoms refined anisotropically are calculated using the formula given by W. C. Hamilton, Acta. Cryst., 1959, 12, 609.

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Chapter 6.

Reactivity of the Heterobimetallic Complexes

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{M}'(\text{CO})_2$ with alkynes ($\text{M}' = \text{Rh}, \text{Ir}$).

6.1 Introduction.

The synthesis and phosphine substitution reactions of the cycloheptatrienyl bridged complexes $(\mu\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{CO})_2$ ($\text{MM}' = \text{FeRh}^2, \text{RuRh}^3, \text{RuIr}^4$) have previously been reported. The incipient coordinative unsaturation provided by the bridging ligand has been proposed to explain the facility of substitution reactions². In this chapter, our study of these bimetallic compounds is continued by investigating the reactivity of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{M}'(\text{CO})_2$ ($\text{M}' = \text{Rh}, \text{Ir}$) with alkynes; a class of organic molecules known to have extensive chemistry with mononuclear and dinuclear complexes⁵. An earlier result⁶ showed that the FeRh complex reacted with the activated acetylene DMAD (dimethylacetylene dicarboxylate) to give cyclotrimerization of the alkyne, a reaction common for transition metal complexes^{5a}. The reactions of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ **1** and $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ **2** with alkynes proved to be metal and alkyne dependent. The reaction of DMAD with the bimetallic complexes was not clean and failed to yield any isolable complexes. However, another activated alkyne, hexafluorobut-2-yne (HFB), gave different products with **1** and **2**, whereas acetylene only gave an isolable product with **1**.

6.2. Results

6.2.1. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ with HFB.

The reaction between $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ (**1**) and hexafluorobut-2-yne (HFB) is very rapid at room temperature. The major product isolated in 45% yield after chromatography is a yellow, air stable solid which is moderately soluble in non-polar organic solvents. The product (**3**), formulated as $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)\text{RuRh}(\text{CO})_5$ on the basis of elemental analysis and mass spectral data contains one HFB ligand added to the starting material. The IR spectrum shows four bands which are shifted to higher frequency with respect to **1**. This is expected for the addition of the electron withdrawing HFB moiety to the metal centres. The ^1H NMR spectrum of **3** is shown in Figure 6.1. There are seven signals for the C_7H_7 ligand indicating that the seven-membered ring is static on the NMR time scale. This is in contrast to the rapid rotation which is observed for **1** at room temperature. Also shown in Figure 6.1 is the ^1H NMR spectrum of the ^{13}C enriched product, in which additional couplings to H3 and H7 are observed. It was determined that these were due to coupling with a CO group on the Rh centre. The ^{13}C and ^{19}F NMR spectra of **3** are shown in Figure 6.2. The ^{19}F NMR spectrum displays two quartets at δ -40 and δ -61 ppm due to the two inequivalent CF_3 groups of the coordinated alkyne. The lower field resonance [$\text{CF}_3(9)$] is also split by an additional coupling to Rh. The ^{13}C NMR data proved to be the most helpful for structure elucidation; two signals for the C_7H_7 ring are observed at relatively low field (δ 125 and δ 138 ppm) indicative of an uncoordinated

Figure 6.1. ^1H NMR Spectra of $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)\text{RuRh}^{(13}\text{CO)}_5$ (a) and $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)\text{RuRh}(\text{CO})_5$ (b). ($\ddagger = \text{CHDCl}_2$)

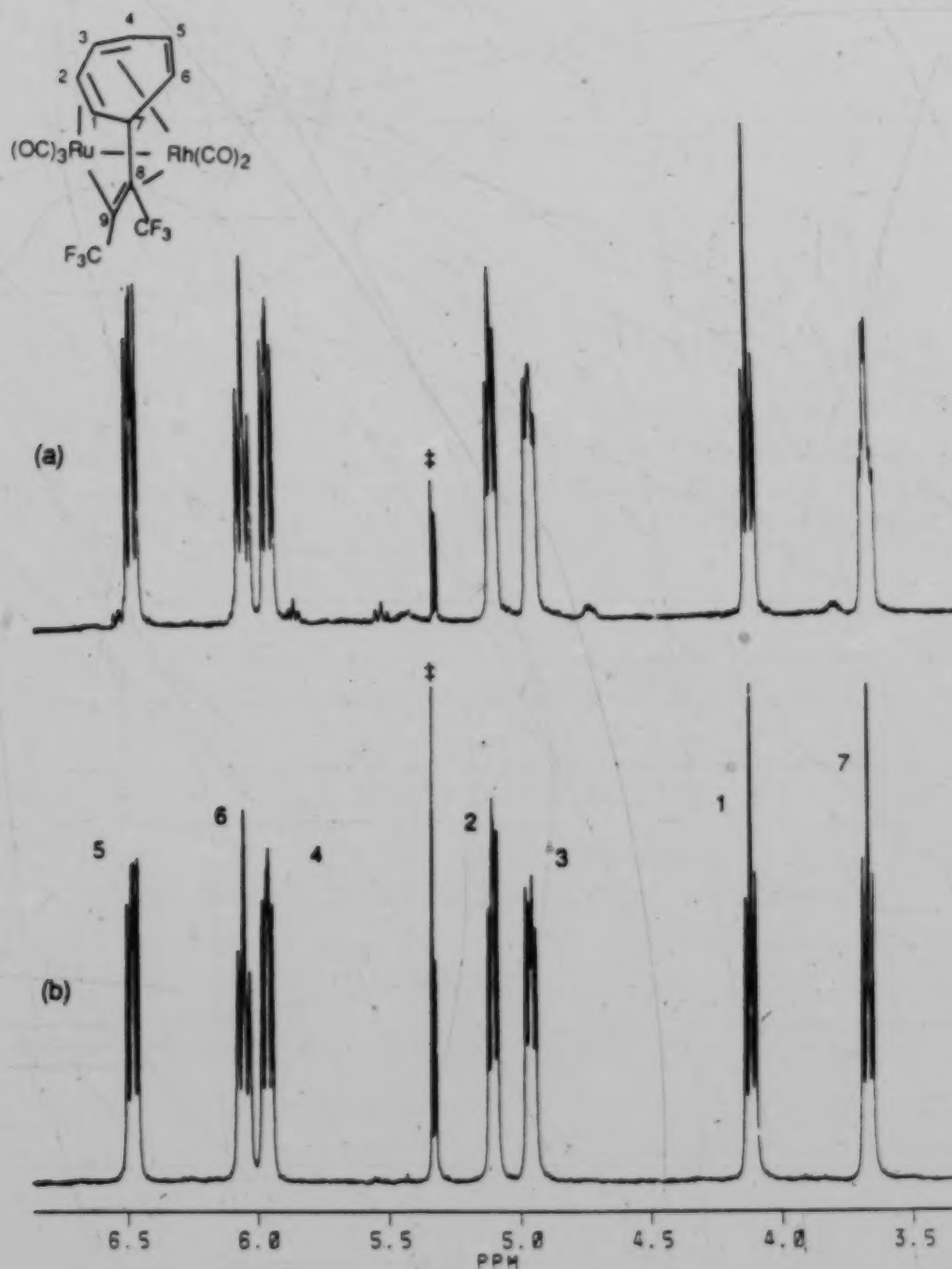
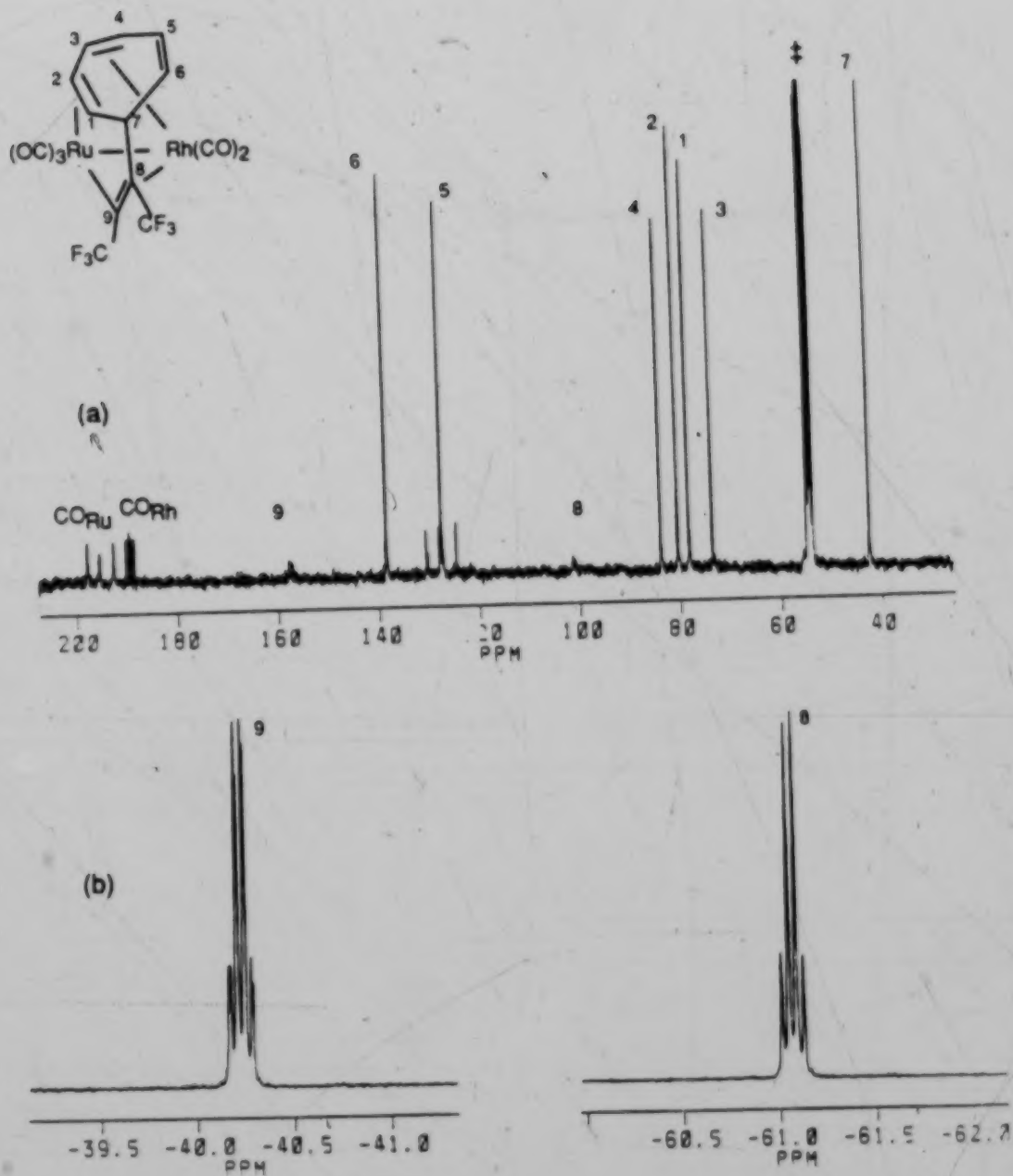


Figure 6.2. ^{13}C (a) and ^{19}F (b) NMR Spectra of 3 ($\ddagger = \text{CHDCl}_2$).

double bond. There are four signals in the region δ 74 - 86 ppm with the final resonance at δ 43 ppm. The observation that the C_7H_7 ligand is static on the NMR time scale is best explained by an insertion of the HFB moiety between a metal and the seven-membered ring. In order to confirm this assignment, and to look at the interaction of the alkyne with the two metals, an X-ray structure determination was carried out.

6.2.2. Molecular Structure of 3.

The structure determination of **3** was carried out by Dr. R. Ball of the Structure Determination Laboratory of this department. The molecular structure of **3** is shown in Figure 6.3, and selected interatomic distances are given in Table 6.1. It can be seen that the acetylenic bond has formally inserted between the Ru centre and one of the carbons of the cycloheptatrienyl ring. The creation of the new C-C and Ru-C bonds has transformed the original acetylenic bond into an olefinic bond, which now has two CF_3 substituents in a cis orientation and is π -bonded to Rh also. The metal-metal bond at 2.7094 (6) Å is considerably shorter than in $(\mu-C_7H_7)Ru(CO)_3Rh(COD)^7$ [2.8878 (6) Å] almost certainly due to the different interaction of the modified bridging ligand. The gain in bonding due to the formation of the μ -vinyl bond is at the expense of the cycloheptatrienyl ligand which now has one double bond uncoordinated (C5-C6). This leaves one double bond coordinated to each metal. The geometry at Ru is best considered as distorted octahedral with a facial $Ru(CO)_3$ fragment. Rhodium is five coordinate trigonal bipyramidal with two olefinic bonds and a CO group in the trigonal plane. The olefinic bond

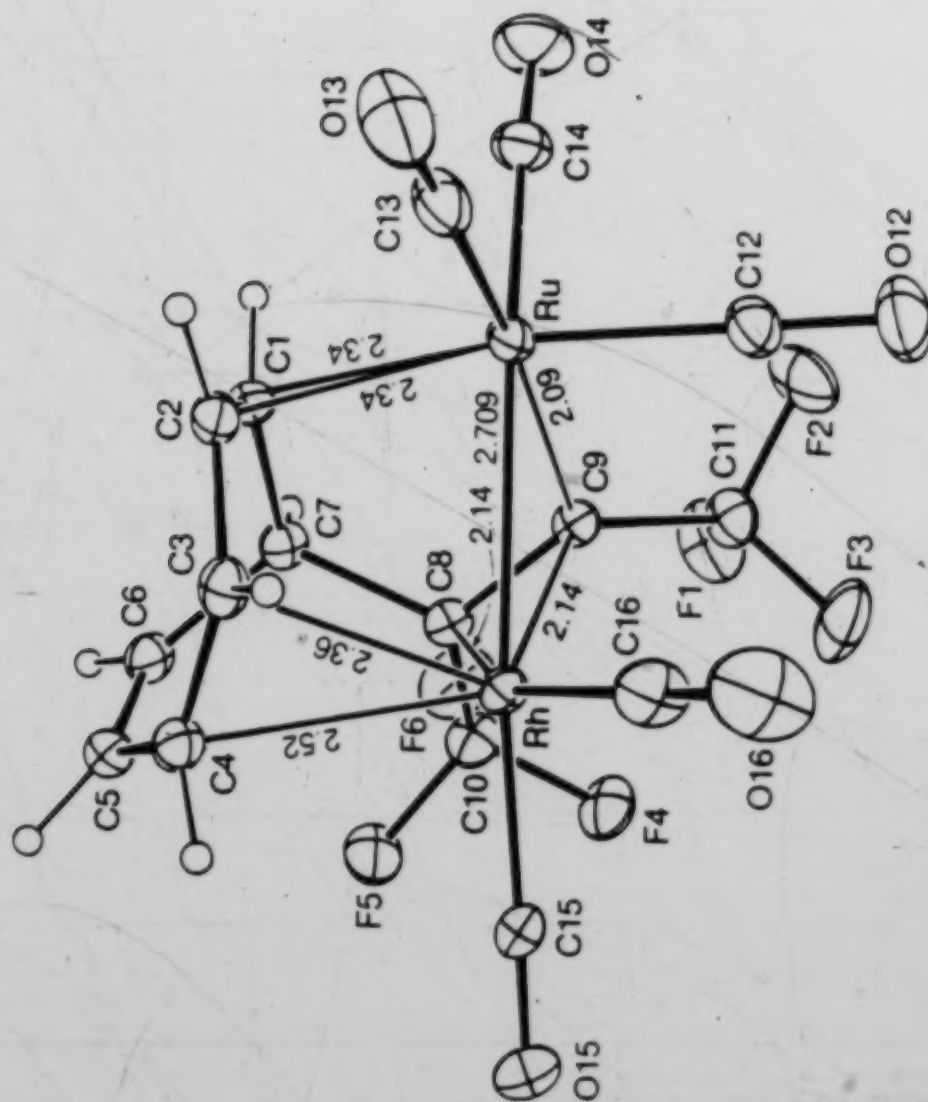


Figure 6.3. Molecular Structure of 3.

Table 6.1. Selected Interatomic Distances in **3**.

Atom1	Atom2	Distance	Atom1	Atom2	Distance
Ru	Rh	2.7094 (6)	C2	C3	1.454 (4)
Rh	C15	1.909 (3)	C2	C1	1.396 (4)
Rh	C16	1.891 (3)	C3	C4	1.369 (4)
Rh	C9	2.144 (3)	C4	C5	1.447 (4)
Rh	C8	2.138 (2)	C5	C6	1.335 (4)
Rh	C3	2.361 (3)	Rh	C4	2.515 (3)
Ru	C12	1.903 (3)	C6	C7	1.492 (4)
Ru	C13	1.959 (3)	C7	C1	1.521 (4)
Ru	C14	1.920 (3)	C7	C8	1.542 (4)
Ru	C2	2.343 (3)	C9	C11	1.510 (4)
Ru	C1	2.376 (3)	C9	C8	1.416 (4)
Ru	C9	2.094 (3)	C8	C10	1.513 (4)
C12	O12	1.131 (4)			
C13	O14	1.119 (4)			
C14	O14	1.130 (4)			
C15	O15	1.129 (4)			
C16	O16	1.130 (4)			

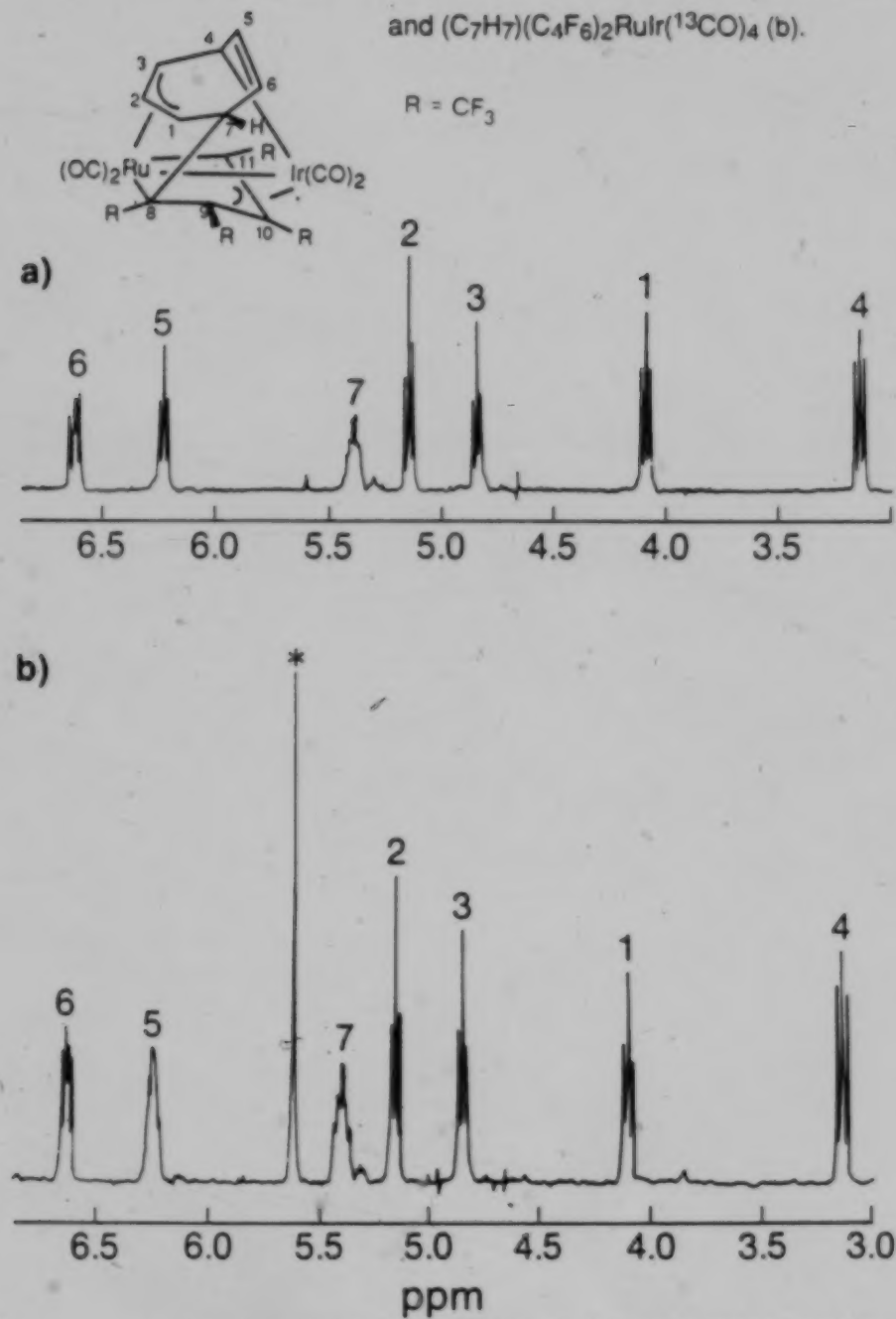
provided by the C₇H₇ ring (C1-C2) is almost perpendicular to the trigonal plane undoubtedly due to steric effects. This is a weak interaction with bond lengths of 2.361 (3) and 2.515 (3) Å to Rh. The bonding between Rh and the olefinic bond created from the HFB insertion, is much stronger with bond lengths of ca. 2.14 Å to both carbons. The new Ru-C9 bond is slightly shorter at 2.094 (3) Å, while the bond lengths between Ru and the two olefinic carbons from the cycloheptatrienyl ring, C1 and C2, are both close to 2.34 Å.

6.2.3. Reaction of (μ-C₇H₇)Ru(CO)₃Ir(CO)₂ with HFB.

In contrast to the rapid reaction observed for RuRh, the reaction of (μ-C₇H₇)Ru(CO)₃Ir(CO)₂ (2) with HFB required thermal activation of 100 °C. This led to the formation of one product which was isolated in 51% yield and formulated as (μ-C₇H₇)(C₄F₆)₂RuIr(CO)₄ (4) on the basis of elemental analysis and mass spectral data. In this reaction, we now see the incorporation of two HFB units into the structure with the loss of one CO ligand.

The ¹H NMR spectrum of 4 (Figure 6.4) again shows seven different resonances at room temperature, indicating a rigid C₇H₇ ring. Typical H-H coupling constants of ca. 8 Hz are observed between adjacent hydrogen atoms, however, one of the signals (H7) shows further splitting (into a quartet) due to coupling with a CF₃ group. These data are again consistent with a structure where at least one HFB ligand has inserted between a metal and the ring as observed in 3. The ¹H NMR spectrum of

Figure 6.4. ^1H NMR Spectra of $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)_2\text{RuIr}(\text{CO})_4$ (a)
and $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)_2\text{RuIr}(^{13}\text{CO})_4$ (b).

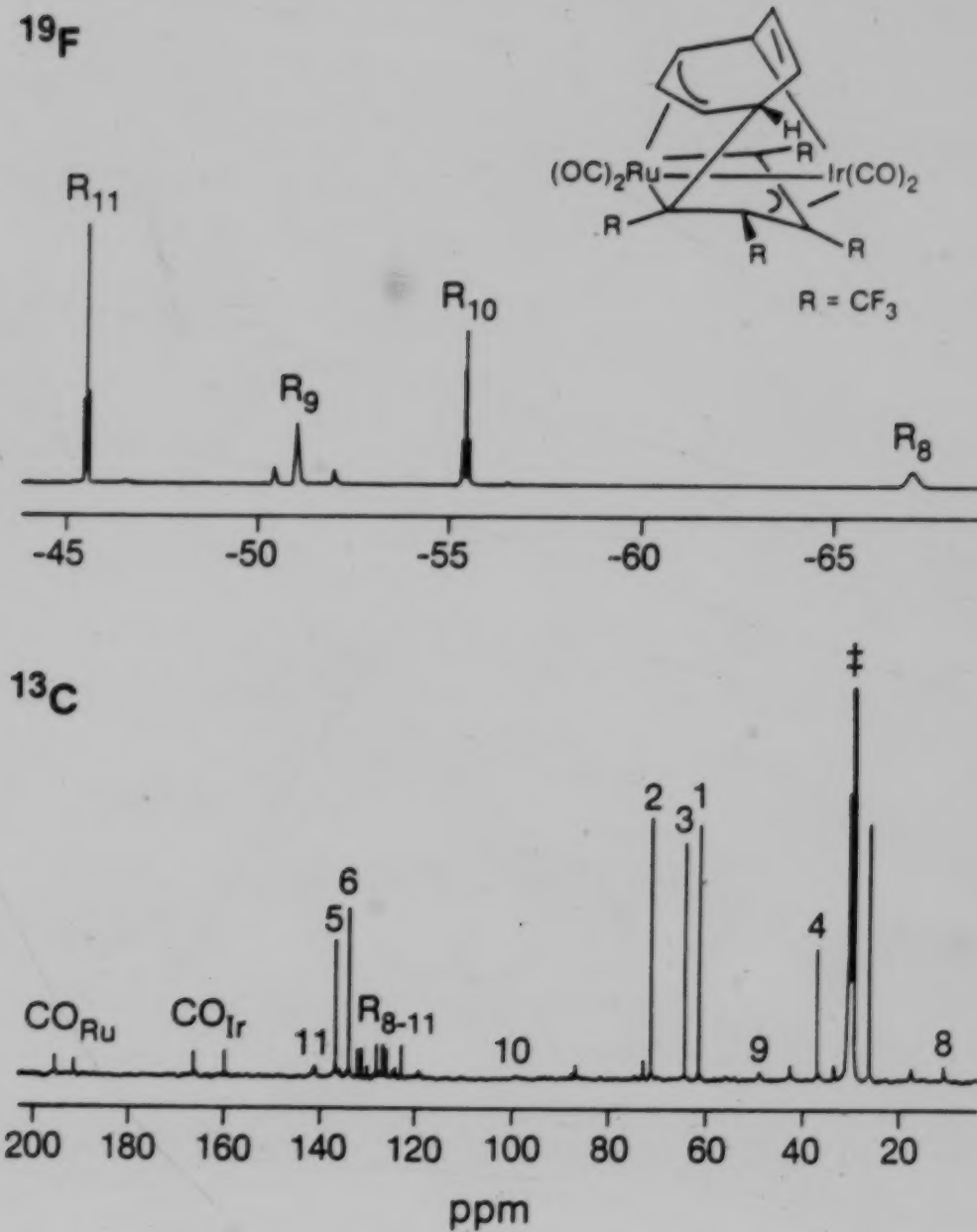


a spectra recorded in acetone- d_6 . * = unidentified impurity.

the ^{13}CO enriched compound is also shown in Figure 6.4. As can be seen, one of the signals (H5) shows additional coupling to one of the carbonyl groups on Ir (at δ 166 ppm). This coupling is most likely a through space coupling, as H5 is a hydrogen on the uncoordinated double bond. The assignments of all the hydrogens were accomplished by a series of homonuclear decoupling experiments.

The room temperature ^{19}F and ^{13}C NMR spectra are shown in Figure 6.5. The assignments for all the spectra were obtained by a series of homonuclear fluorine decoupled spectra (^{19}F spectra) and selective ^1H decoupled ^{13}C spectra. The resonances at δ 136.3 (C5) and 133.7 (C6) in the ^{13}C NMR spectrum again give evidence for one double bond of the original C_7H_7 ring being uncoordinated in the product. For the C_7H_7 ring there are also three resonances at δ 61.1 to 71.1 due to coordinated olefinic carbons, but also two signals at δ 25.9 and 33.2 which are more consistent with saturated carbon atoms. The spectrum also displays signals for two CO groups coordinated to each metal and four signals (C8-11) for the acetylenic carbons. The latter carbons are coupled to more than one CF_3 group and consequently are broad. However, the assignments were confirmed by ^{19}F decoupled ^{13}C NMR spectra. The CF_3 carbons are all quartets between δ 124 and δ 130 with $^1J_{\text{C-F}}$ approximately 280 Hz.

The ^{19}F NMR shows four major peaks of equal intensity at room temperature. Three of these peaks are sharp resonances which, primarily

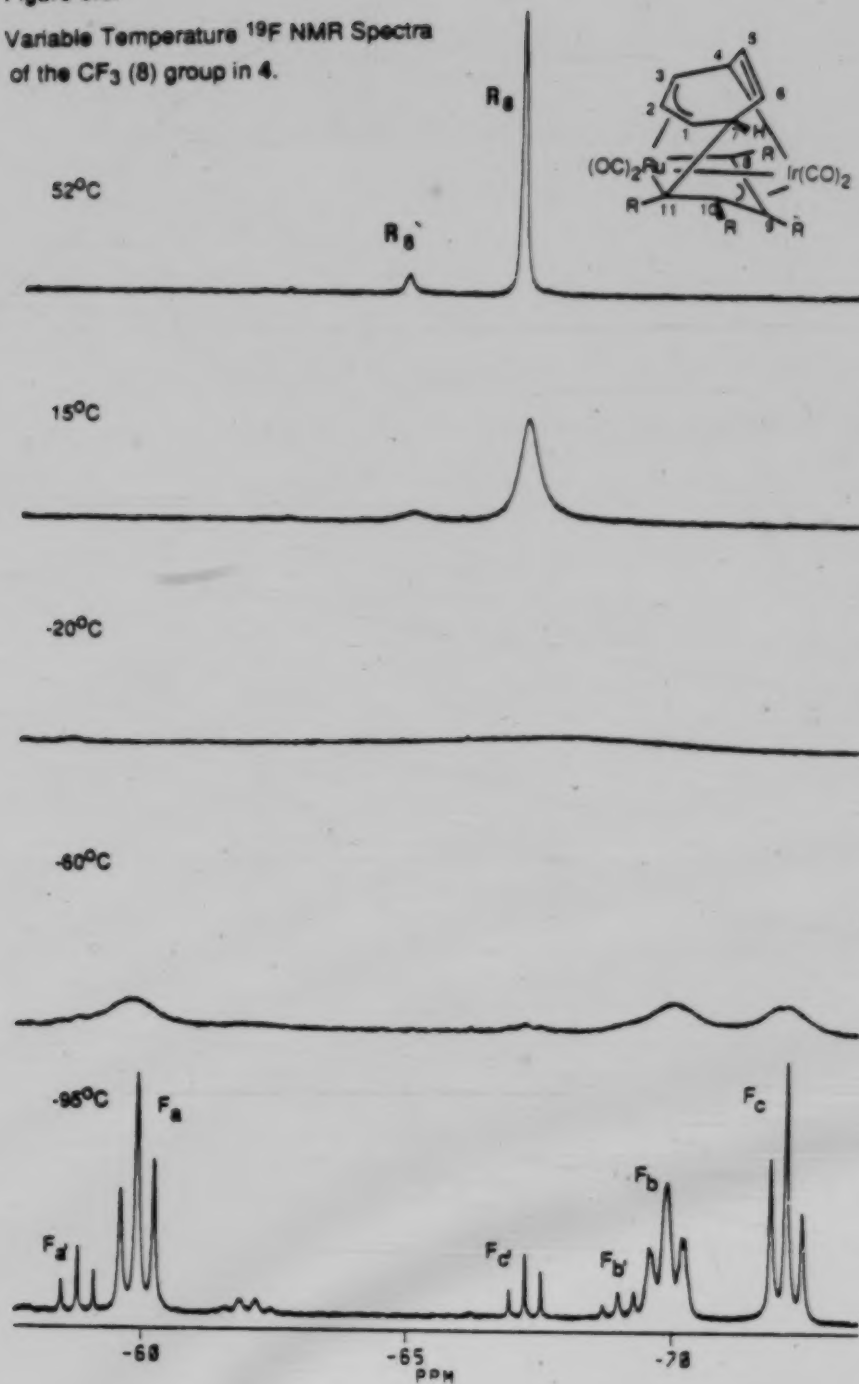
Figure 6.5. ^{19}F (a) and ^{13}C (b) NMR Spectra of **4** ($\ddagger$ = acetone solvate).

as a result of F-F coupling, are split into a quartet ($J_{F-F}=16$ Hz), a septet (clearly caused by 2 quartet couplings of $J_{F-F}=16$ Hz), and a multiplet (qqd, $J_{F-F}=16,9$ Hz, $J_{H-F}=4$ Hz). The fourth peak [$CF_3(8)$] is a broad peak, however, as shown in Figure 6.6, upon cooling to -95 °C, two triplets ($J_{F-F}=115$ Hz) and a triplet of quartets ($J_{F-F}=115,26$ Hz) are observed, due to restricted rotation about a C-C single bond. Upon warming the sample from R.T. to 52 °C, the resonance sharpens however the expected quartet ($J_{F-F}=9$ Hz) is still not attained.

These spectra clearly show that two alkynes have coupled to form a C_4 fragment where one end is attached to the C_7H_7 ligand. Interestingly it is the penultimate CF_3 group [$CF_3(9)$] which shows the F-H coupling. The lowest field signal in the ^{19}F NMR is the quartet and this is assigned to be the other end of the four carbon chain which is bonded to a metal. Further information as to which metal was sought from possible interactions between the CF_3 groups of the C_4 chain and carbonyl groups on the two metal centres. Fortunately, upon enrichment with ^{13}CO , additional couplings to the fluorine resonances are observed, and this is illustrated in Figure 6.7. As shown, the quartet at -45.5 [$CF_3(11)$] shows additional doublet coupling ($J_{C-F} = 2$ Hz). It was confirmed from ^{13}C decoupled ^{19}F NMR spectra that this was due to interaction with a CO group on Ru. From these results, it seems likely that the newly formed bis-alkyne unit has inserted between Ru and the cycloheptatrienyl ring. In Figure 6.7 there are some additional resonances, which are also apparent in the ^{13}C NMR

Figure 6.6.

Variable Temperature ^{19}F NMR Spectra
of the CF_3 (8) group in 4.



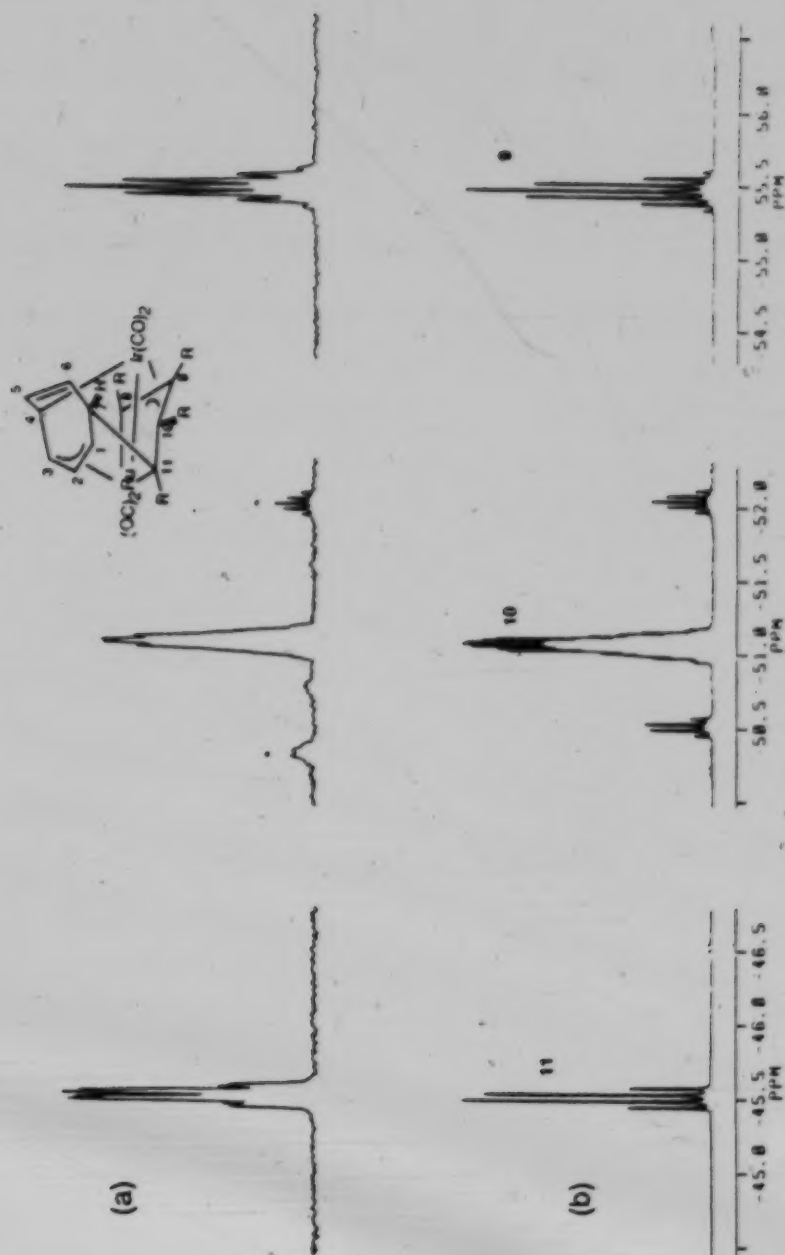


Figure 6.7. ^{19}F NMR Spectra of $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)_2\text{RuIr}(\text{CO})_4$ (a) and $(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)_2\text{RuIr}(\text{CO})_4$ (b).

spectrum, and are marked with asterisks. These are most likely due to another isomeric form of compound **4**. Further comment on the likely structure of **4** is deferred to the discussion.

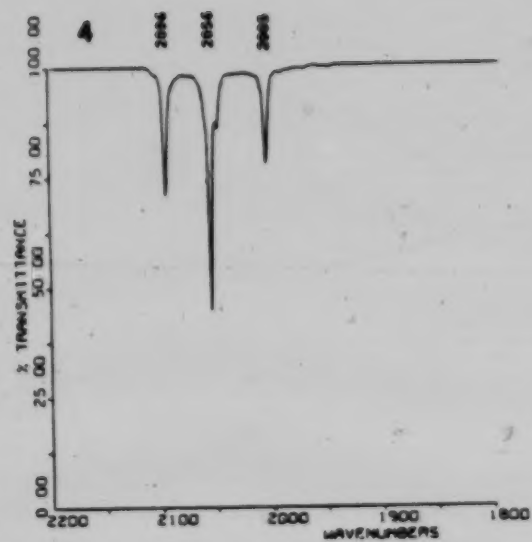
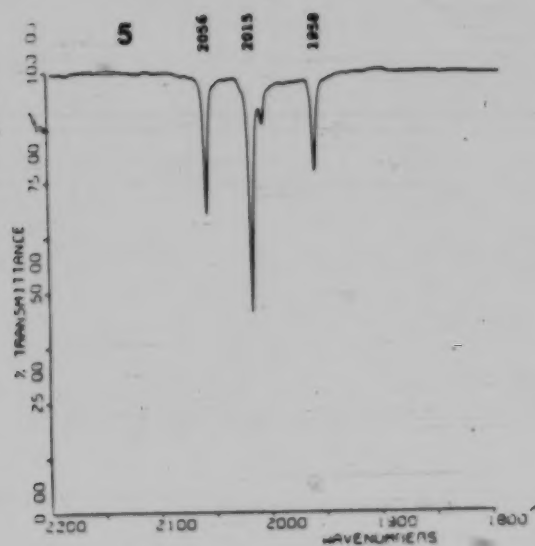
6.2.4. Reactivity of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{M}(\text{COD})$ with HFB.

When the reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{COD})$ (**1b**) with HFB was carried out under the same conditions as the pentacarbonyl compound, no reaction was observed after one hour. This is a severe difference when compared to the rapid reactivity of the pentacarbonyl complex (**1**). When the reaction is allowed to continue for twelve hours at room temperature, some of the starting material is consumed, however no identifiable products are observed. In stark contrast, $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{COD})$ (**2b**) reacts with HFB under very similar conditions as the pentacarbonyl does. Thus when **2b** is reacted with HFB at 105 °C in octane for 3 hours, starting material is completely consumed and the largest yield product observed (14%) is **4**. Clearly this reaction must involve the scavenging of a CO ligand since **2b** has one less carbonyl than the final product (**4**).

6.2.5. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ with C_2H_2 .

The reaction of the RuRh complex **1** with C_2H_2 occurred slowly at room temperature underneath a stream of acetylene gas, to give a black air sensitive solution. The IR spectrum of the black hexane solution in the terminal carbonyl region is shown in Figure 6.8, and as can be seen it is very similar to that of complex **4**. The simple IR spectrum is taken to indicate that the reaction gave primarily one carbonyl containing

Figure 6.8. IR spectra of **4** and **5** in the terminal CO stretching region



product (5). Unfortunately, the product (5) was unstable in the solid state or in solution in the absence of acetylene gas, and as a result could not be isolated in a pure form. The black colouration is most probably due to the formation of polyacetylene. Indeed, metal catalyzed polymerization is not uncommon and is often seen as an undesirable side reaction in attempts to prepare discrete metal-acetylene compounds^{5a,8}.

The similarity of the IR spectra of 4 and 5 in the terminal carbonyl region suggests that these two compounds have closely related geometry. The ¹H and ¹³C NMR spectra of 5 are shown in figure 6-9. Both spectra contain eleven signals for the product. Thus, in similar fashion to the reaction of (μ-C₇H₇)Ru(CO)₃Ir(CO)₂ with HFB, there appears to be two alkyne units and the seven-membered ring intact in the product. A series of homo and heteronuclear decoupling experiments indicated that coupling of two alkyne units and insertion between Ru and the C₇H₇ ring has occurred and allowed the assignments shown in the figure to be made.

6.2.6. Reaction of (μ-C₇H₇)Ru(CO)₃Rh(COD) with C₂H₂.

When the RuRh cyclooctadiene complex (1b) replaced the pentacarbonyl complex (1) as starting material, slightly more forcing conditions were required to enable the reaction to proceed. Thus the reaction was carried out in hexane solution with the pressure of acetylene gas doubled to 15 psi above atmospheric, and the time of reaction

increased to 20 hours. This gave a dark red solution and a black precipitate. The IR spectrum of the solution showed two bands at 2004 and 1941 cm^{-1} indicating that the product obtained in this reaction was different from that obtained from the reaction of the pentacarbonyl complex (1) with C_2H_2 . The new product (6) appeared to be slightly more robust than 5. Thus the solution could be filtered, concentrated, and cooled to -78°C to give an orange supernatant solution from which the product could be precipitated as an orange-red oily residue by the addition of TMS and cooling at -78°C . Attempts to recrystallize the compound were not successful due to decomposition of the product. Hence this compound was only characterized by IR and ^1H NMR spectroscopy. The ^1H NMR data which is given in Table 6.2 shows resonances of the alkyne and C_7H_7 hydrogens which are very similar to those observed for 4. Hence, in contrast to the reaction of 2b with HFB, the COD ligand is not lost in this reaction and the new product is formulated as $(\text{C}_7\text{H}_7)(\text{HC}_2\text{H})_2\text{Ru}(\text{CO})_2\text{Rh}(\text{COD})$ (6).

6.3. Discussion.

6.3.1. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ (1) with HFB.

The RuRh complex undergoes a very rapid reaction with the electrophilic alkyne HFB to give a complex containing one HFB unit inserted between the Ru centre and the seven-membered ring. The two "alkyne" carbons then coordinate to the Rh centre. As a consequence of

Table 6.2 ^1H and ^{13}C NMR Data of $(\text{OC})_2\text{Ru}(\text{C}_7\text{H}_7)(\text{RC}_2\text{R})_2\text{M}'\text{L}_2$ ($\text{M}' = \text{Rh, Ir}; \text{R} = \text{H, CF}_3$)^a.

Compound ^b	$\text{H}_\alpha/\text{C}_\alpha$	$\text{H}_\beta/\text{C}_\beta$	$\text{H}_\gamma/\text{C}_\gamma$	$\text{H}_\delta/\text{C}_\delta$	H_1/C_1	H_2/C_2	H_3/C_3	H_4/C_4	H_5/C_5	H_6/C_6	H_7/C_7
4 ($\text{M}' = \text{Ir}; \text{R} = \text{CF}_3, \text{L} = \text{CO}$)	140.9	98.6	48.5	10.0	61.1	71.1	64.1	33.2	136.3	133.7	25.9
5 ($\text{M}' = \text{Rh}; \text{R} = \text{H}; \text{L} = \text{CO}$)	9.78	7.66	6.08	5.32	0.84	4.38	4.64	3.88	5.42	2.84	1.78
	150.5	110.6	77.5	65.6	52.1	82.6	68.2	75.2	133.4	130.0	34.8
6 ($\text{M}' = \text{Rh}; \text{R} = \text{H}; \text{L}_2 = \text{COD}$)	10.26	7.70	6.29	5.46	1.08	4.82	5.22	4.28	5.84	2.01	2.08

a) $\text{C}_\alpha = \text{C}11; \text{C}_\beta = \text{C}10; \text{C}_\gamma = \text{C}9; \text{C}_\delta = \text{C}8$.b) spectrum in acetone- d_6 (4) spectra in toluene d_8 (5 and 6)

these reaction steps, one double bond of the seven-membered ring is forced to dissociate and the two remaining double bonds are coordinated one to each metal centre. The two CF_3 groups are thus in very different environments. The CF_3 substituent on the carbon which is bonded to both metals [$\text{CF}_3(9)$] is assigned to the low field signal in the ^{19}F NMR (δ -40.2) in accord with the literature⁹. Consistent with this assignment was our observation that in the ^{13}CO enriched material this signal [$\text{CF}_3(9)$] shows additional coupling to a CO group on Ru, whilst the high field signal (δ -61.1) shows further coupling to a CO group on Rh. As expected, in the ^{13}C NMR, the α carbon [$\text{CF}_3(9)$] resonates at considerably lower field than the β carbon [$\text{CF}_3(8)$]¹⁰.

6.3.2. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (2) with HFB.

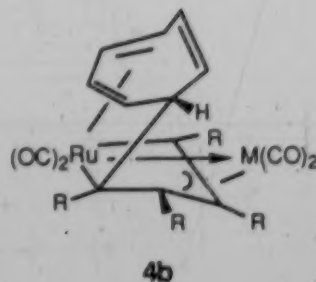
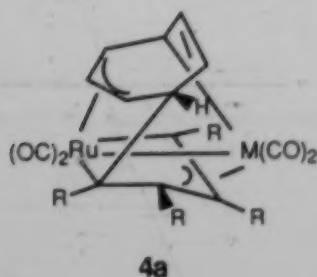
The reaction of HFB with 2 is much less rapid than the analogous reaction with 1, and leads to a different product. In this reaction, two molecules of HFB couple and insert between the seven-membered ring and the Ru centre. However there are several ways this could occur leading to several possible geometries of the final product. In the absence of a crystal structure, F-F coupling constants can be used as a guide to elucidate the arrangement of the coupled organic chain. For example, CF_3 groups in a *cis* orientation on a double bond are known to have much larger coupling constants than when in a *trans* disposition¹¹. In metallacyclopentadiene complexes containing *cis*- CF_3 groups the typical $^5J_{\text{F-F}}$ coupling constant is 12-16 Hz^{12,13}. For complexes containing an open ended metallapentadiene fragment, the coupling constants between

cis-CF₃ groups are more wide ranging in the order of 8 - 15 Hz^{12,14}. In contrast, for a *trans* arrangement of CF₃ groups relative to a double bond the F-F coupling tends to be much smaller¹². Additionally, for complexes containing the M-C(CF₃)=C(CF₃)H functionality, the typical *cis* coupling constant is 12-14.5 Hz⁹, whereas the typical *trans* coupling is 2-2.5 Hz^{9a,11,14a} and sometimes no coupling is observed at all¹⁵.

The ⁵J_{F-F} coupling constants mentioned above for CF₃ groups occupying *cis* positions on a double bond are in a class of many anomalously large five bond F-X coupling constants. To explain this phenomenon it has been proposed that this is most frequently due to a through space mechanism¹⁶. Consistent with this postulate was our observation that after freezing out of rotation of the CF₃(8) group only one F-F coupling of 26 Hz is resolved. Large five bond couplings can also occur between fluorines on a CF₃ group and hydrogens. For example, the coupling between a CH₃ substituent to an adjacent CF₃ group on a metallacyclopentadiene ring is in the region of 2 Hz. In contrast, if the CH₃ group is replaced by an H atom, ⁴J_{F-H} is usually zero¹³. In unison with this, in complex **4** a five bond F-H coupling is observed, whereas the four bond coupling which is possible in **3** and **4** is not observed. This further suggests that a five bond separation between two nuclei is necessary to allow the two nuclei into close proximity such that coupling can occur.

With the help of molecular models, the observed NMR data were used to obtain the most plausible structures for this complex. The ⁵J_{F-F} coupling

constants of 16 Hz between CF_3 groups 11, 10, and 9, are indicative of *cis*- CF_3 groups, and suggest a geometry that is close to that observed in metallacyclopentadiene systems. The consequence of such a rigid *cis* orientation is that the fourth CF_3 group may be brought back to the vicinity of the Ru centre. The F-F coupling constant between $\text{CF}_3(8)$ and $\text{CF}_3(9)$ is 9 Hz. Given these considerations, and in accord with the 18 electron rule the least strained and most likely geometry of the bis-alkyne linkage would contain a bridging allylidene group. As shown below, there are two possible conformations that the molecule can adopt by adjustment of the bonding mode of the seven-membered ring.



In the complex as drawn on the left, both metals attain their 18 electron configuration by formation of a single metal-metal bond. However, a second structure could also exist where two double bonds of the seven-membered ring are coordinated to Ru, and a donor acceptor metal-metal bond from Ru to Ir will allow both metals to obtain the noble gas configuration. Complex **4a** appears to be the less strained product from the molecular models, and would account for the high field resonance (δ

33.2 ppm) in the ^{13}C NMR spectrum which was previously assigned to a saturated carbon atom. Hence **4a** is the preferred structure.

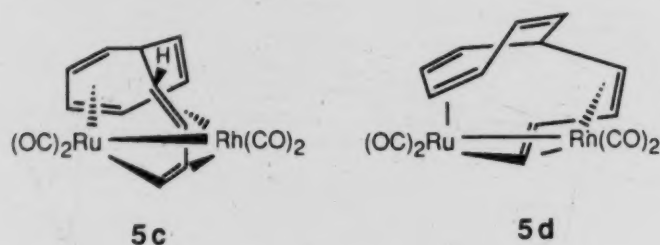
Consistent with the above structure are the known coupling constants and chemical shifts of related bridging allylidene functionalities. There have been complexes reported in the literature which contain CF_3 groups on similar allylic functions as **4a** and which show coupling constants in the range of 14 - 16 Hz¹⁷. The fourth CF_3 group is out of the plane of the pseudo metallacyclopentadiene fragment due to the sp^3 hybridization of C11. This CF_3 group is staggered with respect to the CF_3 group on the adjacent carbon, and the observed F-F coupling between these two groups is 9 Hz. This can be compared to F-F coupling between staggered CF_3 groups on an η^2 -vinyl moiety of ca. 5 Hz in $[\text{Cp}(\text{HFB})(\text{SC}_6\text{H}_4\text{Me-4})\text{W}\{\eta^2\text{-C}(\text{CF}_3)\text{C}(\text{CF}_3)(\text{PEt}_3)\}]$, reported by Davidson¹⁸. The ^{13}C chemical shifts of complexes containing similar bridging allylidene and the very closely related "three alkyne flyover" functionalities are also consistent with this assignment¹⁹. Other support for the proposed geometry include the 2 Hz coupling between a ^{13}CO group on Ir to H5 (see Figure 6.4) and the 4 Hz coupling between $\text{CF}_3(9)$ and H7. Both of these through space interactions could easily occur for **4a**. Additionally, in **4a** one could expect hindrance of the $\text{CF}_3(8)$ group with a CO group on Ru and it is unlikely that any of the other three CF_3 groups would undergo restricted rotation. In summary, for the following reasons we favour structure **4a** to be the accurate description of the geometry of the bis alkyne moiety in **4**:

- (a) The ^{13}C chemical shifts of the α , β , γ , and δ , carbons are in the expected range for bridging allylidene carbons and an alkyl carbon respectively.
- (b) The $^5J_{\text{F-F}}$ coupling constants indicate a cis relationship of the α , β , and γ CF_3 groups, and a staggered relationship of the γ and δ CF_3 groups.
- (c) The through space interactions of the δ CF_3 group with CO_{Ru} and of the γ CF_3 group with H_7 are easily explained by this structure.
- (d) The high field resonance of C5 suggests that the bonding mode of the ring is more appropriately represented by **4a** than by **4b**.

6.3.3. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ with C_2H_2 .

The reaction of **1** with the acetylene, C_2H_2 is much slower than that observed with the electron poor acetylene, HFB. Due to difficulties in isolation, this product was investigated only by its IR and NMR spectra, however, these proved quite informative. According to the IR spectrum (Figure 6-8), a product closely related to complex **4** $[(\text{C}_7\text{H}_7)(\text{HFB})_2\text{Ru}(\text{CO})_2\text{Ir}(\text{CO})_2]$ is obtained. The ^{13}C NMR spectrum clearly showed that only two of the three double bonds of the seven-membered ring were coordinated to a metal. A series of homonuclear proton decoupling experiments showed clearly that two acetylene units had coupled and inserted between the seven-membered ring, and a metal centre. It is assumed that this metal centre is Ru due to the absence of Rh

coupling to the terminal hydrogen atom (H11). The chemical shifts of carbons 11, 10 and 9 are again close to those observed in **4** and in the related bridging allylidene and flyover complexes. However there are several features in the spectra of **5** not consistent with those of **4** (see Table 6.2). For instance, all four of the carbons of the linked alkyne unit show Rh-C coupling. Also, the carbon atoms C4 and C8 which were at 33.2 and 10.0 ppm respectively in **4** are at much lower field in **5** (75.2 and 65.6 respectively). This suggests these carbons are best represented as coordinated olefinic carbons rather than sp^3 hybridized saturated carbon atoms. In order to satisfy these requirements two likely alternative structures (**5c** and **5d**) could be envisioned:



Structure **5c** contains a μ - σ - η^4 -butadiene fragment. This type of bonding of a butadienyl fragment to a dinuclear compound has been previously observed and structurally characterized in $[(\text{dippe})\text{Rh}]_2(\mu\text{-}\eta^4\text{-}\sigma\text{-C}_4\text{H}_5)(\mu\text{-H})^{20}$ [dippe = 1,2-bis(diisopropylphosphino)ethane]. The construction of **5c** is based on that structure. In this case the four carbons of the diene fragment are close to being planar and occupy an s-cis configuration. An alternative structure (**5d**) can also be imagined where the diene occupies an s-trans configuration. Apart from the configuration

of the diene unit, the other main difference between **5c** and **5d** is that the hydrogen atoms on the double bonds between C11 and C10 and between C9 and C8 are in a cis-trans arrangement in **5c** but are trans-cis in **5d**. Structures containing a cis-cis relationship or a trans-trans relationship were ruled out as neither would meet the requirements set by the ^{13}C NMR spectrum. In order to elucidate which structural alternative (**5c** or **5d**) may most accurately describe the bonding in **5**, a survey of H-H coupling constants in coordinated diene systems was carried out.

Both configurations of the diene unit (s-cis and s-trans) have been noted previously in $\text{Cp}_2\text{Zr}(\text{butadiene})^{21}$, $\text{CpMo}(\text{NO})(\text{butadiene})^{22}$ and $\text{CpMo}(\text{CO})_2(\text{butadiene})^+$ complexes²³. Typical H-H coupling constants in these complexes (where α and δ represent the terminal atoms) are s-cis: $J_{\text{H}\alpha-\text{H}\beta} = J_{\text{H}\gamma-\text{H}\delta} = 8-10.5$ (cis-H), $10.5 - 12.5$ (trans-H), $J_{\text{H}\beta-\text{H}\gamma} = 6-11$; s-trans: $J_{\text{H}\alpha-\text{H}\beta} = J_{\text{H}\gamma-\text{H}\delta} = 6-8$ (cis-H), $7-16.5$ (trans-H), $J_{\text{H}\beta-\text{H}\gamma} = 7-16$. The magnitude of the coupling constants is very dependent on the system and the bonding of the diene fragment to the transition metal. For example, the $\text{H}\beta-\text{H}\gamma$ coupling constant is much larger for $\text{Cp}_2\text{Zr}(\text{butadiene})$ complexes than for $\text{CpMo}(\text{CO})_2(\text{butadiene})^+$ complexes, possibly due to an increased double bond character of the central C β -C γ bond in the former complexes.²⁴ The observed coupling constants for **5** ($J_{\text{H}\alpha-\text{H}\beta} = J_{\text{H}\gamma-\text{H}\delta} = 11$, $J_{\text{H}\beta-\text{H}\gamma} = 8$) are therefore consistent with the formulation of a diene unit containing two separate double bonds with little double bond character between them. This may be expected as the structure is probably twisted due to the coordination requirements and may be better viewed as two

olefinic units rather than a conjugated diene functionality. Apart from this observation, however it is difficult to make any further predictions. On the basis of a precedential compound structurally related to **5c** we very tentatively favour **5c** over **5d**.

In summary, **5** clearly has a structure related to **4**, where two acetylene units have coupled and inserted between Ru and the C₇H₇ ring, however for this complex we tentatively suggest that the adopted structure is closer to **5c** than to **4a** for the following reasons:

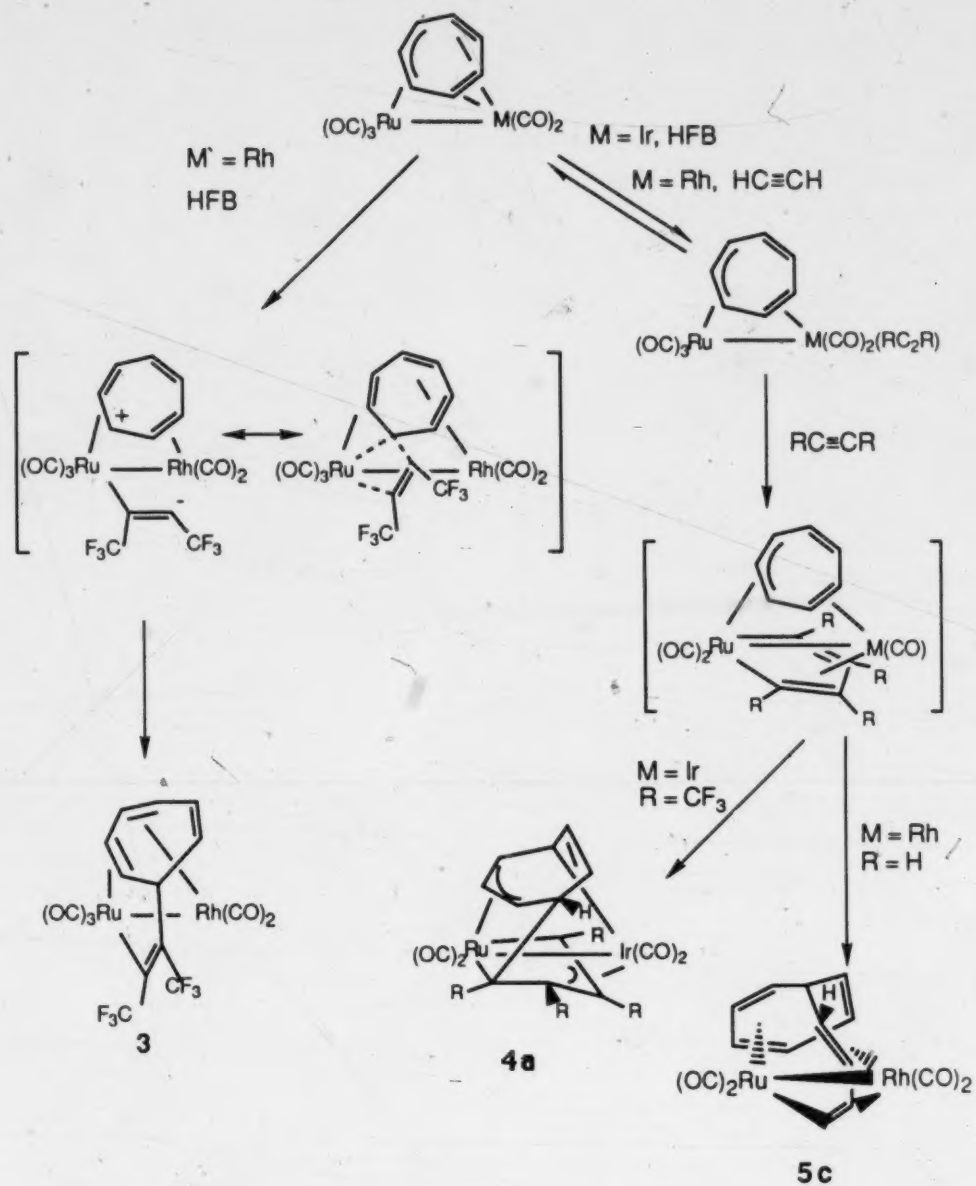
- (a) The observation of Rh-C coupling constants of 8, 3, 8, and 8 Hz for carbons 11 - 8 and no Rh coupling to carbons of the seven-membered ring.
- (b) In the ¹³C NMR spectrum, the resonances for C11 and C10 are close to those expected for **4a** or **4b**. However, the resonance for C9 and especially that for C8 are at much lower field than in **4**, and are more characteristic of a coordinated olefin^{10b}. Similarly the H9 and H8 resonances are more consistent with a coordinated olefin^{14a,b} than a bridging allylidene unit¹⁷.
- (c) The H-H coupling constants of the C₄ fragment suggest a diene unit with not much double bond character of the central C10-C9 bond.

(d) There are few similarities in the ^1H and ^{13}C NMR spectra of the C_7H_7 ring between **4** and **5**. In particular, the chemical shifts of the outer carbons of the diene fragment coordinated to Ru show large differences (**5**; C1; 52.1, C4; 75.2. **4**; C1; 61.1, C4; 33.2). Other noteworthy features of **5** which are not reflected in the spectra of **4** are the surprisingly high field shifts of H1 (0.84) and the uncoordinated olefinic proton H6 (2.84).

6.3.4. Possible Explanation for the Observed Reactivity.

The rapid reaction of **1** with HFB can be explained by rapid electrophilic attack of the HFB moiety at the electron rich Ru centre, Scheme 6.1. The insertion could occur via an ionic intermediate or by a concerted pathway. This reaction is closely related to the insertion of HFB into a Ru-Cp bond observed by Stone²⁵.

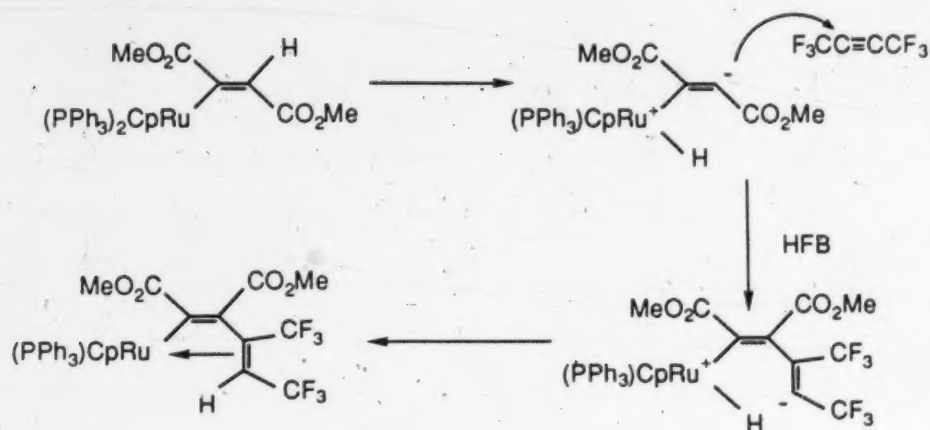
In contrast, the analogous RuIr complex (**2**) requires thermal activation of 100 °C to enable a reaction to occur. The presence of an Ir centre instead of the 2nd row Rh centre clearly leads to the increased inertness. The most logical initial step in the RuIr reaction at 100 °C is coordination of an HFB unit to one of the metal centres. Due to the lack of a product analogous to **3** [$(\text{C}_7\text{H}_7)(\text{C}_4\text{F}_6)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$] and the inability of **3** to insert cleanly one more equivalent of HFB upon heating, the next step is apparently not insertion of the alkyne moiety between Ru and the seven-membered ring. Instead upon subsequent approach of a second HFB moiety to the dinuclear complex, coupling between the two alkynes and insertion between Ru and the seven-membered ring must occur to obtain

Scheme 6.1. Possible reactivity of alkynes with **3** and **4**.

the observed product. Clearly the formation of the RuIr complex (**4**) is far more complicated than the path followed in the RuRh reaction. One obvious contender for the formation of **4a** involves a metallacyclopentadiene complex as shown in the scheme. Numerous examples of similar complexes are known, and further insertion reactions of these complexes with extra alkynes are well documented^{5,13a,28}. Hence the observed C-C bond formation in our complex is easily envisioned.

The reaction between **1** [$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$] and HC_2H follows a similar path to the reaction between RuIr and HFB although the geometry of the final product appears to be different. This is probably a consequence of the different steric requirements of the alkynes in the coupling step. The effects of the very different electronic demands of HFB and C_2H_2 cannot be entirely ruled out, however. A very similar reaction was observed between the cyclooctadiene complex **1b** and HC_2H although the final product in this reaction maintained the COD moiety. Thus these reactions are alkyne dependent as well as metal dependent. The decrease in the observed rate of reaction, and reversal of reactivity going from HFB to C_2H_2 suggests that the path followed for the reaction of **1** with HFB reaction is heavily favoured for alkynes with electron withdrawing substituents. This is consistent with the ionic intermediate shown in the scheme. Zwitterionic intermediates have been previously proposed in related C-C bond forming reactions²⁶. In one related

example, such an intermediate is proposed to undergo addition to an HFB ligand²⁷:



6.4. Summary.

$(\mu-C_7H_7)Ru(CO)_3Rh(CO)_2$ (**1**) undergoes a rapid addition reaction with the activated alkyne HFB. However the analogous reaction of $(\mu-C_7H_7)Ru(CO)_3Rh(COD)$ (**1b**) produces no such product. Clearly replacement of two CO groups on Rh with the bulky COD ligand blocks the reaction pathway. Alternatively, $(\mu-C_7H_7)Ru(CO)_3Ir(CO)_2$ reacts with HFB under thermal conditions with loss of 1 CO ligand to give the complicated product **4**. In this case substitution of two CO groups on Ir with the COD ligand in the starting material has little effect on the reactivity and the same product (**4**) is produced in lower yield. Thus the first step in the reactions of the $RuIr$ complexes with HFB may be substitution of a ligand at the Ir centre. Also consistent with this proposal was the observation that no

product analogous to **4** is produced when **3** is heated in the presence of HFB. This implies that insertion of one HFB moiety between Ru as the first step in these reactions followed by a second insertion is not likely. These observations suggest that replacement of Rh with Ir in the starting pentacarbonyl compounds $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{M}(\text{CO})_2$ decreases the nucleophilicity of the Ru centre and hence alters the reaction pathway.

6.5. Experimental.

6.5.1. General Techniques and Reagents, Chapter 6.

Hexafluorobut-2-yne (HFB) was bought from S. C. M. Speciality Chemicals. Acetylene was purchased from Matheson Gas Products Canada, and passed through a cold trap at -78°C to remove small amounts of acetone. For ^{19}F NMR, CFCI_3 was used as a calculated external standard. $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ (**1**) was made according to the literature^{2a}. The preparation of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (**2**) is described in Chapter 2. The complete solid-state structural determination of compound **3** was carried out by Dr. R. G. Ball of the Structure Determination Laboratory of this department. Some relevant information from the structure report is included in this thesis. Further information including listings of observed and calculated structure factors may be obtained from Dr. J. Takats of this department.

6.5.2. Preparation of $(\mu\text{-C}_7\text{H}_7)(\mu\text{-C}_4\text{F}_6)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ (**3**).

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ (25 mg) was dissolved in hexane (10 ml) and freeze-thaw degassed. A slow stream of HFB was then bubbled through the reaction mixture for 1 minute. The red-brown solution was then stirred for 5 minutes with no colour change. The solvent was then removed to leave a brown residue which was chromatographed on a silica gel column (3 cm x 1.5 cm) eluting with hexane. The major band which is an orange colour is collected and crystallized from hexane to leave yellow-orange crystals of **3** (16 mg, 45 %).

Anal. Calcd. for $C_{16}H_7F_6O_5RhRu$: C; 32.18, H; 1.35. Found: C; 32.35, H; 1.22.

M. S. (90 °C, 16 eV, 70 eV) $P^+ = 598$, $P^+ - n(CO)$, $n = 0 - 5$.

IR (ν_{CO} , hexane); 2089 (m), 2056 (s), 2035 (m), 2015 (m).

^1H NMR (22 °C, CD_2Cl_2) δ 3.66 (1H,t,H7, $J_{H7-H1}=J_{H6-H7}=7$), 4.12

(1H,t,H1, $J_{H1-H2}=J_{H7-H1}=7$), 4.96 (1H,dd,H3, $J_{H2-H3}=5.5$, $J_{H3-H4}=9.5$), 5.10

(1H,dd,H2, $J_{H1-H2}=J_{H2-H3}=5.5$), 5.96 (1H,dd,H4, $J_{H3-H4}=9.5$, $J_{H4-H5}=6.5$)

6.04 (1H,dd,H6, $J_{H5-H6}=9.5$, $J_{H6-H7}=7$), 6.48 (1H,dd,H5, $J_{H4-H5}=6.5$, $J_{H5-H6}=9.5$).

^{13}C NMR (22 °C, CD_2Cl_2) δ 42.0 (C7), 73.2 (C3), 77.9 (C1), 80.1 (C2),

83.5 (C4), 127.2 (C5), 138.3 (C6), 101.1 (m, $C\beta$), 125.5 (q, $J_{C-F}=220$ Hz, $C(CF_3\beta)$),

129.0 (q, $J_{C-F}=220$ Hz, $C(CF_3\alpha)$), 157.6 (m, $C\alpha$), 188.8

(d, CO_{Rh} , $J_{Rh-C}=80$ Hz), 189.6 (d, CO_{Rh} , $J_{Rh-C}=70$ Hz), 192.6 (s, CO_{Ru}),

195.4 (s, CO_{Ru}), 197.7 (s, CO_{Ru})

^{19}F NMR (22 °C, CD_2Cl_2) δ -61.1 (3F,q, $J_{F-F}=14$ Hz, $CF_3\beta$), -40.2 (3F,dq, $J_{F-F}=14$ Hz, $J_{Rh-F}=3$ Hz, $CF_3\alpha$).

6.5.3. Solid-State Structure Determination of **3**.

The structure determination was carried out by Dr. R. G. Ball of the Structure Determination Laboratory of this department. The following information was extracted from SDL report number SR: 200111-03-87. A yellow crystal of **3** was mounted on an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using MoK α radiation with a graphite crystal, incident beam monochromator. The automatic peak search and reflection indexing programs in conjunction with a cell reduction program showed the crystal to be monoclinic and from the systematic absences of $h0l$, $h + l$ odd; $0k0$, k odd the space group was determined to be $P2_1/n$, (an alternative setting of $P2_1/c$). Cell constants were obtained from a least-squares refinement of the setting angles of 24 reflections in the range $14 < 2\theta < 28^\circ$. The various crystal parameters are given in Table 6.3. The structure was solved using the direct methods program MITHRIL²⁹ which gave the positional parameters for the Rh and Ru atoms. The remaining non-hydrogen atoms were located by the usual combination of least-squares refinement and difference Fourier synthesis³⁰. An empirical absorption correction was applied, using the Fourier filter scheme of Walker and Stuart³¹. The positional and thermal parameters of the non-hydrogen atoms are given in Table 6.4.

Table 6.3. Crystallographic Data for Compound 3.

		3
empirical formula		C ₁₆ H ₇ F ₆ O ₅ RhRu
colour of crystal		yellow
crystal dimensions (mm)		0.20 x 0.24 x 0.43
space group		P2 ₁ /n
cell dimensions	a (Å)	9.875(2)
	b (Å)	13.583(2)
	c (Å)	13.636(4)
	β (°)	102.09(2)
Z (Molecules/cell)		4
V (Å ³)		1788
d (calcd), (g/cm ³)		2.218
wavelength (Å)		0.71069
mol wt		597.20
linear abs coeff (cm ⁻¹)		18.22
detector to sample dist (cm)		20.5
scan type		ω -2 θ
scan rate (deg/min)		10.1 - 2.6
scan width (deg)		0.70 + 0.35tan(θ)
data collection 2 θ limit(deg)		55.00
aperture size (mm)		2.40 x 4.0
total no. of reflctns collected		4518
no. of unique intensities		4232
no. with I > 3.0 σ (I)		3369
observations/variables ratio		3369/262
R1		0.023
R2		0.033
goodness of fit for the last cycle		1.22
corrections applied		absorption correction
data collection index range		h,k, $\pm$ l

Table 6.4. Positional ($\times 10^4$) and Thermal ($\times 10^2$) Parameters for 3.

Atom	x	y	z	$U, \text{\AA}^2$
Rh	6333.8(2)	2603.7(2)	7865.3(1)	3.168(6)
Ru	3759.0(2)	1983.2(2)	7966.5(2)	3.436(6)
O12	3232(3)	3815(2)	9104(2)	8.05(9)
O13	3839(3)	829(2)	9920(2)	8.27(9)
O14	718(3)	1666(3)	6992(3)	8.6(1)
O15	8985(3)	3520(2)	7489(3)	8.2(1)
O16	6682(3)	3471(3)	9942(2)	10.4(1)
C12	3426(3)	3139(2)	8669(2)	5.1(1)
C13	3772(3)	1242(3)	9201(2)	5.31(9)
C14	1843(3)	1755(3)	7373(3)	5.3(1)
C15	7979(3)	3192(2)	7606(3)	4.73(9)
C16	6572(4)	3117(3)	9179(2)	5.7(1)
C2	5075(3)	581(2)	7800(2)	4.02(8)
C3	6474(3)	904(2)	8237(2)	4.00(8)
C4	7505(3)	984(2)	7708(2)	4.40(9)
C5	7384(3)	686(2)	6674(2)	4.58(9)
C6	6248(3)	760(2)	5948(2)	4.50(9)
C7	4993(3)	1316(2)	6075(2)	3.81(8)
C1	4352(3)	791(2)	6852(2)	3.87(8)
C9	4370(3)	2878(2)	6886(2)	3.47(7)
C11	3693(3)	3864(2)	6602(2)	5.1(1)
C8	5265(3)	2411(2)	6344(2)	3.49(7)
C10	5828(4)	2941(3)	5538(2)	5.3(1)
F1	3395(3)	4022(2)	5619(2)	8.85(9)
F2	2479(2)	3959(2)	6866(2)	8.76(8)
F3	4410(3)	4638(2)	6995(2)	9.3(1)
F4	6073(2)	3895(1)	5710(1)	6.47(7)
F5	7039(2)	2572(2)	5416(2)	7.17(7)
F6	4985(3)	2865(2)	4632(2)	8.9(1)

The equivalent isotropic thermal parameter is given by: $U = 1/3 \sum r_i^2$ where r_i are the root-mean-square amplitudes of vibration.

6.5.4. Preparation of $(\mu\text{-C}_7\text{H}_7)(\text{C}_4\text{F}_6)_2\text{RuIr}(\text{CO})_4$ (4).

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Ir}(\text{CO})_2$ (50 mg) was dissolved in octane (10 ml) and freeze-thaw degassed. One atmosphere of HFB gas was then introduced to the frozen solution which was warmed to 100 °C and stirred for 2 hours. The solvent was removed from the dark orange solution to leave an orange-brown residue which was washed with hexane (4 ml) and chromatographed on a silica gel column (9 cm x 1.5 cm) eluting with 40 % CH_2Cl_2 /hexane. There appeared to be two major bands. The first band is yellow, which is followed by a green band, however the IR and NMR spectra of the two bands showed few differences. Both fractions were combined, and the solvent was removed to leave a cream solid which was recrystallized from CH_2Cl_2 /hexane to give pale yellow-green crystals of 4 (40 mg, 51 %).

Anal. Calcd. for $\text{C}_{19}\text{H}_7\text{F}_{12}\text{OIrRu}$: C, 27.81, H, 0.85, Found, C, 27.74, H, 0.84.

M. S. (FAB), $P^+ = 822$, $P^+ - n(\text{CO})$, $n = 0 - 4$.

IR (ν_{CO} , hexane); 2095 (m), 2055 (s), 2049 (w), 2005 (m).

^1H NMR (22 °C, acetone d_6); δ 3.13 (1H, dd, H4, $J_{\text{H}3\text{-H}4}=7.5$, $J_{\text{H}4\text{-H}5}=9$), 4.08

(1H, t, $J_{\text{H}1\text{-H}2}=J_{\text{H}7\text{-H}1}=7.5$), 4.94 (1H, t, H3, $J_{\text{H}2\text{-H}3}=J_{\text{H}3\text{-H}4}=7.5$), 5.14

(1H, t, H2, $J_{\text{H}1\text{-H}2}=J_{\text{H}2\text{-H}3}=7.5$), 5.38 (1H, m, H7), 6.23 (1H, t, H5, $J_{\text{H}4\text{-H}5}=J_{\text{H}5\text{-H}6}=9$), 6.62 (1H, dd, H6, $J_{\text{H}5\text{-H}6}=9$, $J_{\text{H}6\text{-H}7}=6$)

^{13}C NMR (22 °C, acetone- d_6); δ 10.0 (q, C8, $J_{\text{C-F}}=30$), 25.9 (s, C7), 33.2

(s, C4), 48.5 (m, C9), 61.1 (s, C1), 64.1 (s, C3), 71.1 (s, C2), 98.6 (m, C10),

124.0 (q, CF_3 , $J_{\text{C-F}}=280$), 124.5 (q, CF_3 , $J_{\text{C-F}}=280$), 129.5 (q, CF_3 , $J_{\text{C-F}}=275$),

130.0 (q, CF₃, J_{C-F}=280), 133.7 (s, C₆), 136.3 (s, C₅), 159.8 (s, CO_{Ru}), 166.2 (s, CO_{Ru}), 191.4 (s, CO_{Ir}), 195.3 (s, CO_{Ir}).

¹⁹F NMR (22 °C, acetone-d₆); δ -67.0 (br, CF₃δ), -55.4 (sp, J=16Hz, CF₃β), -51.2 (qqd, J_{F-F}=14,9Hz, J_{H7-F}=4Hz, CF₃γ), -45.5 (q, J=16Hz, CF₃α). (-95 °C); -72.3 (t, J_{F-F}=115), -70.3 (qt, ²J_{F-F}=115, ⁵J_{F-F}=25), -58.9 (t, J_{F-F}=115).

6.5.5. Reaction of (μ-C₇H₇)Ru(CO)₃Rh(COD) with HFB.

(μ-C₇H₇)Ru(CO)₃Rh(COD) (**1b**) (10 mg) was dissolved in hexane (10 ml) to give an orange solution. The solution was degassed and then introduced to 1 atmosphere of HFB gas. The solution was then stirred for 12 hours at room temperature with no colour change. An IR spectrum of the reaction mixture at this point showed approximately half of the starting material had been consumed. The solvent was removed and the residue was redissolved in hexane (5 ml) and rapidly cooled to -78 °C for 15 minutes. The supernatant solution was then transferred to a separate vessel. An IR spectrum of this solution showed only bands due to the starting RuRh(COD). Extraction of the residue in hexane gave no carbonyl containing compounds. The residue did dissolve in CH₂Cl₂ however the IR spectrum showed several bands all of very low intensity.

6.5.6. Reaction of (μ-C₇H₇)Ru(CO)₃Ir(COD) with HFB.

(μ-C₇H₇)Ru(CO)₃Ir(COD) (**2b**) (30 mg, 0.052 mmoles) was dissolved in toluene (5 ml) and freeze-thaw degassed. The frozen solution was then introduced to one atmosphere of HFB gas and the closed reaction vessel was placed in an oil bath which was heated to 118 °C. The solution was

stirred for 1 hour, cooled and then the solvent was removed. The residue was dissolved in hexane and filtered to a separate reaction vessel. An IR spectrum of the extract showed primarily **4**. Chromatography and crystallization of **4** as described above yielded 7 mg (14 %) of **4**.

6.5.7. Preparation of $(\mu\text{-C}_7\text{H}_7)(\text{C}_2\text{H}_2)_2\text{RuRh}(\text{CO})_4$ (**5**).

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ (30 mg) was dissolved in toluene (5 ml) and freeze-thaw degassed three times. The frozen red solution was then put under 1 atmosphere of HC_2H and warmed to room temperature. The solution was then stirred for 2 hours to give a black solution. The solvent was then removed and the dark residue was evacuated for 1 further minute before it was reintroduced to an acetylene atmosphere. Toluene- d_8 (0.6 ml) was then added to the reaction vessel. The dark black solution was then filtered by canula into an NMR tube under acetylene pressure.

IR (ν_{CO} , hexane); 2055 (m), 2014 (s), 2004 (w), 1958 (m).

^1H NMR (22 °C, toluene- d_8); δ 0.84 (dd, H_1 , $J_{\text{H}_1\text{-H}_2}=8$, $J_{\text{H}_1\text{-H}_3}=1.5$), 1.78 (d, H_7 , $J_{\text{H}_7\text{-H}_8}=8$), 2.84 (d, H_6 , $J_{\text{H}_5\text{-H}_6}=8$), 3.88 (t, H_4 , $J_{\text{H}_3\text{-H}_4}=J_{\text{H}_4\text{-H}_5}=8$), 4.38 (dd, H_2 , $J_{\text{H}_1\text{-H}_2}=8$, $J_{\text{H}_2\text{-H}_3}=5$), 4.64 (ddd, H_3 , $J_{\text{H}_1\text{-H}_3}=1.5$, $J_{\text{H}_2\text{-H}_3}=5$, $J_{\text{H}_3\text{-H}_4}=8$), 5.32 (dd, H_8 , $J_{\text{H}_7\text{-H}_8}=8$, $J_{\text{H}_8\text{-H}_9}=11$), 5.42 (t, H_5 , $J_{\text{H}_4\text{-H}_5}=J_{\text{H}_5\text{-H}_6}=8$), 6.08 (dd, H_9 , $J_{\text{H}_8\text{-H}_9}=11$, $J_{\text{H}_9\text{-H}_{10}}=7$), 7.66 (ddd, H_{10} , $J_{\text{H}_9\text{-H}_{10}}=7$, $J_{\text{H}_{10}\text{-H}_{11}}=11$, $J_{\text{H}_{10}\text{-Rh}}=2$), 9.78 (d, H_{11} , $J_{\text{H}_{10}\text{-H}_{11}}=11$).

^{13}C NMR (22 °C, toluene- d_8); δ 34.8 (s, C_7), 52.1 (s, C_1), 65.6 (d, C_8 , $J_{\text{C}_8\text{-Rh}}=7$), 68.2 (s, C_3), 75.2 (s, C_4), 77.5 (d, C_9 , $J_{\text{C}_9\text{-Rh}}=8$), 82.6 (s, C_2), 110.6 (d, C_2 , $J_{\text{C}_2\text{-Rh}}=2.4$), 130.0 (s, C_6), 133.4 (s, C_5), 150.5 (d, C_{11} , $J_{\text{C}_{11}\text{-Rh}}=8$).

186.4 (d, CO_{Rh} , $J_{\text{C-Rh}}=61$), 190.4 (d, CO_{Rh} , $J_{\text{C-Rh}}=73$), 194.7 (s, CO_{Ru}), 196.6 (s, CO_{Ru}).

6.5.8. Reaction of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{COD})$ with C_2H_2 .

$(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{COD})$ (26 mg) was dissolved in hexane (18 ml) and placed in a 100 ml 'pop-bottle' which was connected to a vacuum line and an acetylene tank. The red solution was then freeze-thaw degassed and introduced to 15 psi above atmospheric of HC_2H . The solution was then stirred for 24 hours before the pressure was released. The solution was then filtered, concentrated to 3 ml and cooled to -78°C for 16 hours. The orange supernatant solution was then separated from the brown residue and crystallized from hexane/ $(\text{Me}_3\text{SiO})_2$ at -30°C to give an orange-red residue which was used for the NMR sample.

IR (ν_{CO} , hexane); 2004 (s) 1941 (s) cm^{-1} .

^1H NMR (22°C , toluene- d_8); δ 1.08 (dd, H_1 , $J_{\text{H}_1\text{-H}_2}=8$, $J_{\text{H}_1\text{-H}_3}=1.5$), 1.96 (m, 2H, COD), 2.01 (1H, m, H_6), 2.08 (d, H_7 , $J_{\text{H}_7\text{-H}_8}=8$), 2.10 (m, 2H, COD) 2.56 (m, 2H, COD), 2.76 (m, 1H, COD), 2.94 (m, 2H, COD), 3.62 (m, 1H, COD), 4.20 (m, 1H, COD), 4.28 (t, H_4 , $J_{\text{H}_3\text{-H}_4}=J_{\text{H}_4\text{-H}_5}=8$), 4.70 (m, 2H, COD), 4.82 (dd, H_2 , $J_{\text{H}_1\text{-H}_2}=8$, $J_{\text{H}_2\text{-H}_3}=5$), 5.22 (dd, H_3 , $J_{\text{H}_1\text{-H}_3}=1.5$, $J_{\text{H}_2\text{-H}_3}=5$, $J_{\text{H}_3\text{-H}_4}=8$), 5.46 (dd, H_8 , $J_{\text{H}_7\text{-H}_8}=8$, $J_{\text{H}_8\text{-H}_9}=11$), 5.84 (t, H_5 , $J_{\text{H}_4\text{-H}_5}=J_{\text{H}_5\text{-H}_6}=8$), 6.29 (dd, H_9 , $J_{\text{H}_8\text{-H}_9}=11$), 7.70 (dd, H_{10} , $J_{\text{H}_9\text{-H}_{10}}=7$, $J_{\text{H}_{10}\text{-H}_{11}}=11$), 10.26 (d, H_{11} , $J_{\text{H}_{10}\text{-H}_{11}}=11$).

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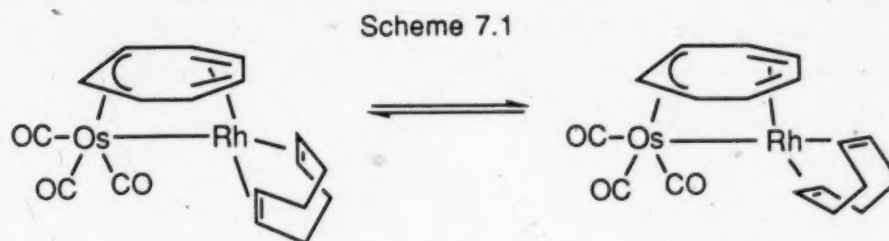
Chapter 7.

Fluxional Processes and Trends in Properties within a Series of Cycloheptatrienyl Bridged Heterobimetallic Complexes.

7.1. Properties of the Cyclooctadiene Complexes, $(\mu\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{COD})$.

As a result of the studies reported in this thesis, the series of cis heterobimetallic complexes $(\mu\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{COD})$ ($\text{M} = \text{Fe, Ru, Os}$; $\text{M}' = \text{Rh, Ir}$) is complete. Within this series of complexes, the inertness of the isolated complexes increases as either metal triad is descended. One way that this can be demonstrated is by looking at the substitution reaction of the COD ligand at the group 9 metal centres. For example carbonylation of the RuIr^1 and FeIr^2 cyclooctadiene complexes occurs only upon thermal heating whereas this reaction occurs readily at room temperature for the related RuRh^3 and FeRh^4 complexes. More interesting was the observation that the same effect, albeit less dramatic, was seen when the group 8 metal was changed. For example, reaction times for the FeRh^4 , RuRh^3 and OsRh^5 complexes at room temperature are 5 mins, 90 mins, and 150 minutes respectively. The net effect thus appears to be a greater amount of electron donation from the $\text{M}(\text{CO})_3$ to the $\text{M}'(\text{COD})$ fragment as the M triad is descended.

A more quantitative method of comparing the strengths of the M'-COD interaction is by comparing the free energies of activation for rotation of the COD group. This process, which is shown diagrammatically in Scheme 7.1, involves change in geometry at the M' centre from square pyramidal to trigonal bipyramidal⁴ and back to the original ground state structure.



The free energies of activation for COD rotation were obtained from the approximate expression, equation 7.1, which relates the free energy of activation, $\Delta G^\ddagger$, coalescence temperature, T_c , and chemical shift separation $\Delta\nu$ (Hz) for a pair of equal singlets undergoing exchange⁶.

$$\Delta G^\ddagger = 4.57T_c[9.97 + \log(T_c/\Delta\nu)] \quad (7-1)$$

The coalescence temperature and chemical shift separation between exchanging pairs of olefinic or aliphatic carbon/hydrogen signals were obtained from variable temperature NMR studies. Although it is recognized that approximating the ^1H NMR signals as singlets is strictly not correct, the errors introduced by neglecting H-H coupling are less than the error due to the uncertainties in T_c (± 5 K). Besides, in view of the approximations, we have much more reliance on the trends exhibited by

$\Delta G^\ddagger$ than the absolute values obtained for a specific compound. The resultant free energies of activation are listed in Table 7.1. As expected, when one replaces Rh(COD) with Ir(COD) there is a considerable stabilization of the metal-olefin bonding as evidenced by an increase of 4 kcal/mole in $\Delta G^\ddagger$. What is more interesting and pleasing to see is the effect of the non-participating metal. When the spectator metal is changed from Fe to Ru to Os there is a sequential increase in $\Delta G^\ddagger$ of 1 kcal/mole. This trend parallels the observed trend in the average ^{13}C chemical shift of the olefinic carbon atoms resonance to higher field upon descending the triad. Shifts to higher fields in the ^{13}C NMR spectrum of coordinated olefinic ligands have been associated with enhanced metal to ligand back-bonding⁷ and hence stronger metal-olefin bonds.

The other two fluxional processes occurring in these complexes involve the metal tricarbonyl unit, and the seven membered ring. As mentioned in Chapter 4, these processes appear to be related and are explained in Scheme 7.2.

Scheme 7.2



Table 7.1. ^{13}C NMR Data and $\Delta G^\ddagger$ for COD rotation in *cis*-($\mu\text{-C}_7\text{H}_7$) $\text{M}(\text{CO})_3\text{M}'(\text{COD})$ compounds ($\text{M} = \text{Fe, Ru, Os}$; $\text{M}' = \text{Rh, Ir}$).

M-M'	δC_0 , ave	T_c , °C ^a	$\Delta\delta/\text{Hz}$	$\Delta G^\ddagger/\text{kcal/mole}^b$
Os-Ir	63.3	95 (Ha)	130	18
Ru-Ir	64.7	80 (Ca)	180	17
Fe-Ir	68.0	60 (Co)	80	16
Os-Rh	75.2	15 (Co)	100	14
Ru-Rh	80.9	0 (Ca)	100	13
Fe-Rh	84.2	-30 (Ha)	140	12

a Coalescence of: Ha; aliphatic hydrogens, Ca; aliphatic carbons, Co; olefinic carbons, of COD ligand.

b Errors in $\Delta G^\ddagger$ are approximately 1 kcal/mole.

The carbonyl scrambling process is best considered as a trigonal twist of the octahedral $\text{M}(\text{CO})_3$ group. In the trigonal prismatic intermediate involved in this process, one of the CO ligands comes into close proximity of the second metal centre thus allowing the formation of a bridging intermediate. This would also involve concomitant change in bonding mode of the C_7H_7 ring. In this mechanism, the two exchange processes are coupled and hence each is influenced by the nature of both metal centres. Thus on going from complex 3 (c-OsIr) to 2 (c-OsRh), a dramatic effect on the carbonyl scrambling in $\text{Os}(\text{CO})_3$ is observed (see Chapter 4). In contrast the local carbonyl scrambling in both complexes 1 (c-RuIr) and

2 (c-OsRh) is frozen out at about - 80 °C, despite the fact that one is considering a Ru(CO)₃ group in **1** (see Chapter 2) versus an Os(CO)₃ group in **2**.

7.2. Rotation of the C₇H₇ ring in dinuclear (μ-η³,η⁴-C₇H₇) complexes.

In this thesis the preparation of the cis-cycloheptatrienyl bridged heterobimetallic compounds (μ-C₇H₇)M(CO)₃M'(COD) [MM' = RuIr (**1**), OsRh (**2**), OsIr (**3**)] have been described. In all three cases, the low temperature ¹H and ¹³C NMR spectra have displayed signals for the static molecule. This was quite surprising as the number of examples of bimetallic compounds which contain a *cis*-(μ-η³,η⁴-cycloheptatrienyl) ring in which freezing out of metal migration around the ring is observed is still quite limited. Table 7.2 gives the chemical shifts of the ring hydrogens in those bimetallic compounds where the slow limiting spectrum has been attained. Apart from the series of complexes prepared in our group a *cis*-CoCr complex, Cp*Co(μ-η³,η⁴-C₇H₇)(μ-H)Cr(CO)₃ (**4**), and a *trans*-FeMo complex, (OC)₃Fe(μ-η³,η⁴-C₇H₇)Mo(CO)₂Cp (**5**) are also included in the table. Whilst the data set is still limited, there are three trends which can be found:

- a) For both *trans* complexes, the slow limiting spectrum is obtained relatively easily. Also, the average chemical shift for the ring hydrogens is at lower field in the *trans* compounds than in the *cis* complexes.

Table 7.2. ^1H and ^{13}C NMR data for bimetallic ($\mu\text{-}\eta^3\text{-}\eta^4\text{-C}_7\text{H}_7$) Complexes.

Compound	T ^a	$\Delta G^\ddagger$	δH1	δH2	δH3	δH4	$\delta\text{H}_{\text{ave}}$	$\delta\text{C}_{\text{ave}}$
3 (c-OsIr)	-30	14 ^b	3.07	3.30	2.03	3.81	3.34	-
2b (c-OsRh)	-100	10 ^c	4.10	3.56	2.54	4.50	3.68	80.8
1 (c-RuIr)	-100	8.4 ^c	3.54	3.76	2.80	4.72	3.82	60.0
4 (c-CoCr) ^d	-73	-	1.55	2.58	2.68	4.07	2.92	68.2
5 (t-FeMo) ^d	-71	13 ^c	4.82	4.37	3.77	5.37	4.57	-
2a (t-OsRh)	-50	12 ^b	4.90	4.24	3.88	4.74	4.43	-
6 (c-FeRh)	-	-	-	-	-	-	3.76	-
7 (c-RuRh)	-	-	-	-	-	-	3.75	-
8 (c-FeIr)	-	-	-	-	-	-	3.82	-

a Temperature at which the slow limiting spectrum was recorded.

b $\Delta G^\ddagger$ (for C_7H_7 rotation) obtained from spin inversion experiments (see Chapter 4)

c $\Delta G^\ddagger$ obtained from simulation of spectral data [± 1 kcal/mole (approx)].

d **4** is $\text{Cp}^*\text{Co}(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)(\mu\text{-H})\text{Cr}(\text{CO})_3$ ⁸; **5** is $(\text{OC})_3\text{Fe}(\mu\text{-}\eta^3, \eta^4\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{Cp}$ ⁹; Spectrum in CDCl_3 /toluene- d_8 (4:1).

e **6** is $(\mu\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3\text{Rh}(\text{COD})^3$, **7** is $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{COD})^4$, **8** is $(\mu\text{-C}_7\text{H}_7)\text{Fe}(\text{CO})_3\text{Ir}(\text{COD})^2$.

b) For cis complexes **3** and **4** in which the limiting spectrum has been obtained relatively easily, δH_{ave} is at relatively high field.

c) For complexes containing identical ligands, the activation energy for ring rotation increases as the metal triad is descended. In the cis-cycloheptatrienyl bridged complexes of FeRh, FeIr, and RuRh, complexes ring rotation has not been frozen out upon cooling, and values of δH_{ave} are close to 3.8.

A possible explanation for these observations is that for cis complexes of the lower transition series there is increased back-bonding from the metal into antibonding molecular orbitals of the C_7H_7 ligand. This should result in increasing the metal-ligand bond strength and consequently decreasing fluxional behaviour. This is likely as increases in metal-ligand bond strengths upon descending a triad are well known¹⁰. The CoCr complex **4** is an exception to this rule. This may be the result of different electronic contributions to the seven-membered ring as a consequence of the bridging hydrogen atom. Alternatively the presence of the highly electron donating ligand, Cp^* may allow strong back-bonding to the seven-membered ring such that its rotation may be stopped. The high field shift of the ring hydrogens in complexes **3** and **4** is consistent with this proposal as an increase in backbonding from the metals to the seven-membered ring should lead to an increase in sp^3 character of the ring hydrogens. There is some precedent to these claims as both olefin rotation barriers have been shown to increase¹¹, and the bond order of

unsaturated organic substrates coordinated to a transition metal, have been shown to decrease upon descending a transition metal triad¹².

7.3. General Conclusions.

As discussed in this chapter, both metals appear to have an effect on the local and global fluxional behaviour of the complexes $(\mu\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{COD})$ ($\text{M} = \text{Fe, Ru, Os}$; $\text{M}' = \text{Rh, Ir}$). This effect is also extended to the chemical properties of these complexes. Thus, in Chapter 6 it was observed that the reactivity of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{CO})_2$ with HFB at the Ru centre was not replicated when Rh was replaced by Ir, almost certainly due to electronic reasons. Substitution of COD with carbonyl groups appeared to have little effect on the fluxional behaviour of the bimetallic compounds (see Chapter 2), although a dramatic effect in the reactivity of $(\mu\text{-C}_7\text{H}_7)\text{Ru}(\text{CO})_3\text{Rh}(\text{COD})$ with HFB was observed. This was presumably due to steric reasons. Upon coordination of a PPh_3 ligand to the group 9 metal centre a change in the electronic properties of the bimetallic complexes occurs such that the expected compounds, $(\mu\text{-C}_7\text{H}_7)\text{M}(\text{CO})_3\text{M}'(\text{CO})\text{PPh}_3$ exist in equilibrium with the carbonyl bridged compounds, $(\mu\text{-C}_7\text{H}_7)(\mu\text{-CO})\text{M}(\text{CO})_2\text{M}'(\text{CO})(\text{PPh}_3)$ in which there is a reversal of the bonding mode of the C_7H_7 ligand. In these phosphine substituted complexes, ($\text{M} = \text{Fe, Ru}$, $\text{M}' = \text{Rh, Ir}$), the fluxional behaviour is greater than the parent pentacarbonyl complexes as evidenced by the appearance of relatively facile global carbonyl scrambling. However, a more surprising result is the trend in free energies of activation ($\text{Fe} > \text{Ru}$

and $Rh > Ir$) for the intermetallic carbonyl scrambling process. A possible explanation for this phenomenon was offered in Chapter 2.

7.4. Experimental.

The synthesis, NMR Data and deduction of activation parameters for complexes **2a**, **2b**, and **3** were described in Chapter 4. The synthesis of **1** was described in Chapter 2. The values of the activation parameters for **1** were calculated by the method which was described in Chapter 4. The observed and calculated rate constants for **1** are given in Table 7.3, and the deduced activation parameters are given below.

Table 7.3. Observed and Calculated Rate Constants for the 1,2-metal migration around the seven-membered ring in **1**.

Temperature	Rate Constant	
	Observed	Calculated
213	15000	16353.71
203	7000	6436.10
183	800	740.32
173	250	109.13
163	50	50.77
158	20	23.42

Activation Parameters for **1** $\Delta H^\ddagger$; 7.60 (0.53) kcal/mol, $\Delta S^\ddagger$; -2.92 (2.90) cal/mol K (standard deviation in parenthesis). This gives a calculated value of $\Delta G^\ddagger$ of 8.5 kcal/mole.

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